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AMERICAN LEATHER CHEMISTS ASSOCIATION

VOL. LI MAY 1956 No. 5

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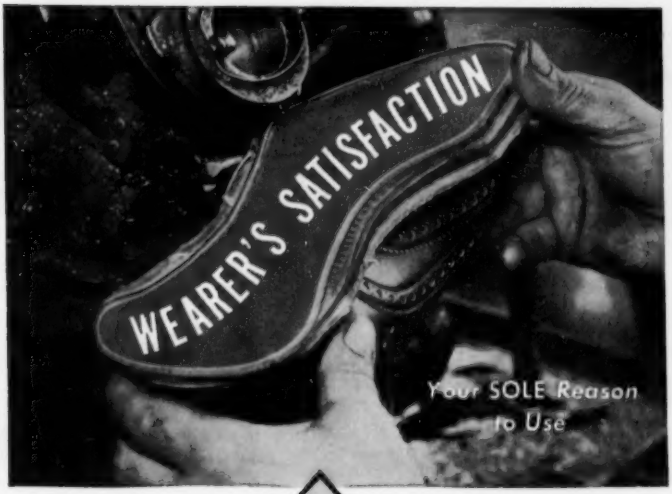

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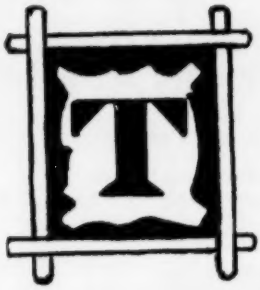

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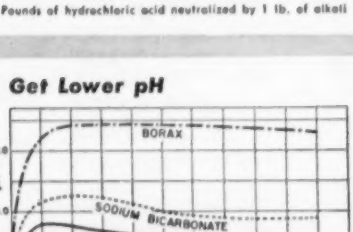

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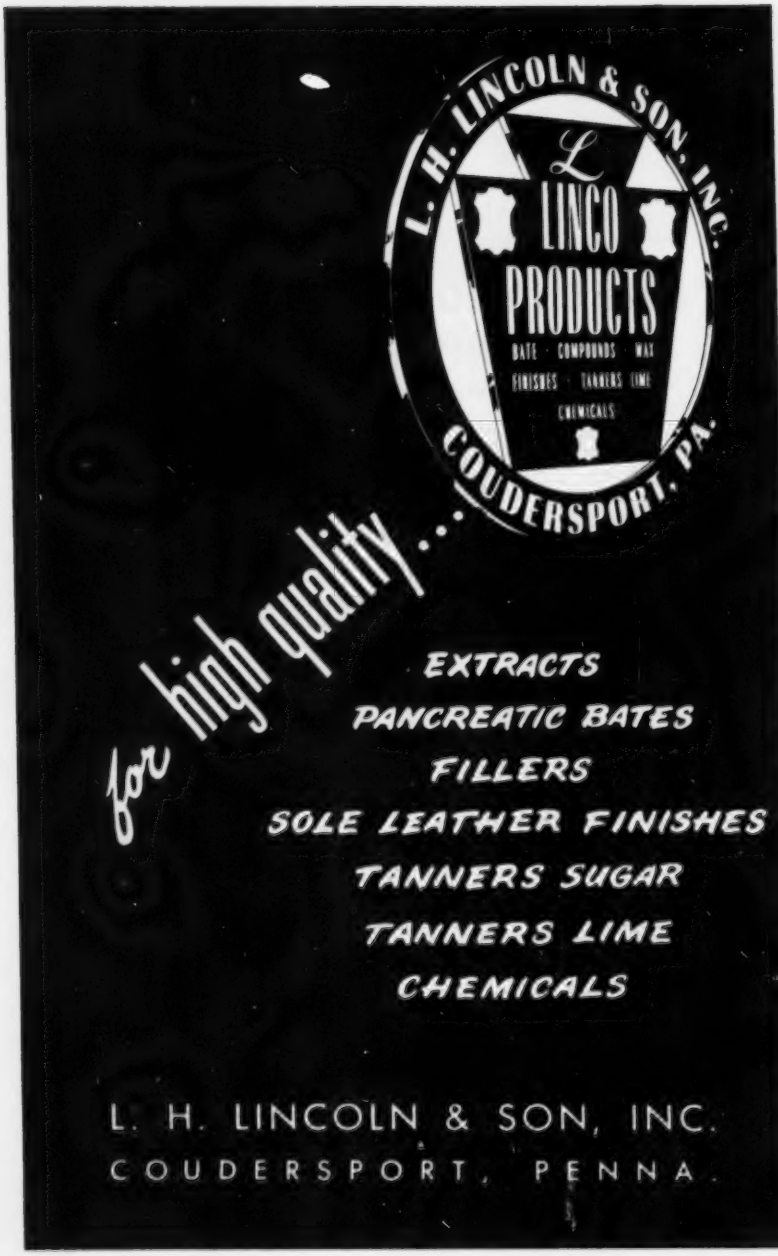
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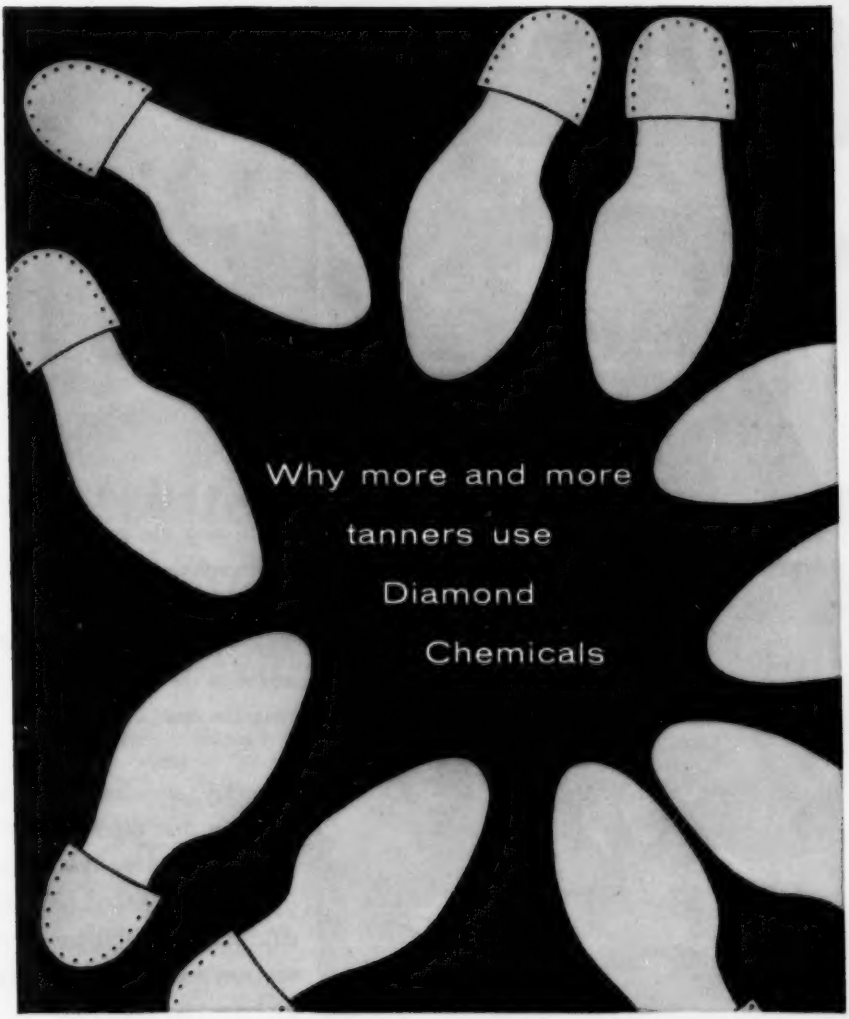

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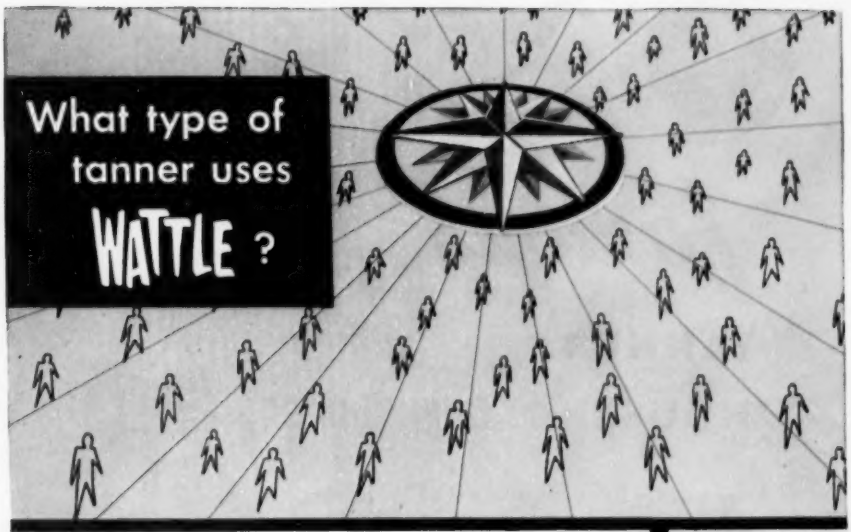

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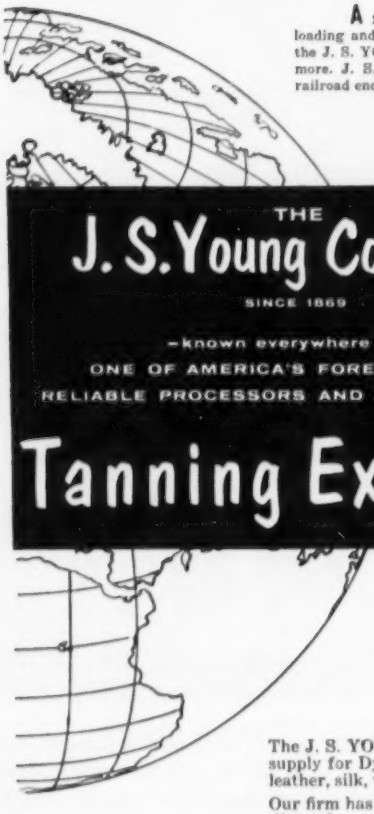

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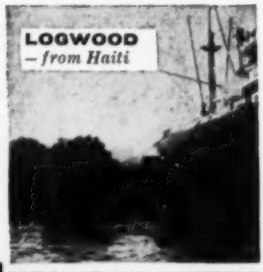

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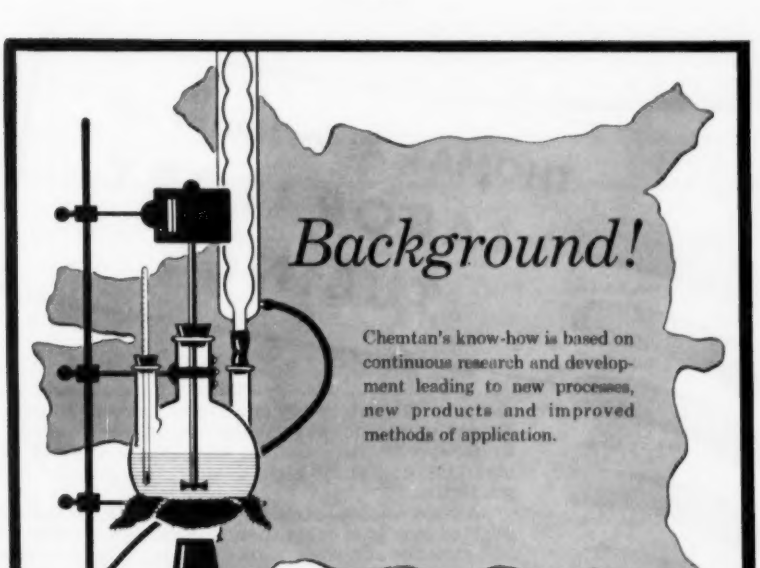
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YOUR NEW EDITORS

The grievous—and wholly unforeseen—loss, which our Association suffered when our honored and beloved Dean Williams was taken from us, brought an end to an editorial era, matched by few scientific journals. From 1910 to 1955, this Journal had but two editors—William K. Alsop from 1910 to 1936, and Dean Williams from 1936 to 1955—and these two men had been so closely associated for many years before Williams assumed the editorship that the change meant little more than a minor revision of the Journal's masthead. The devoted and able service that these men, Alsop and Williams, gave to the Association through forty-five long, and often trying, years has set a mark that will be difficult indeed for their successors to equal.

The name and services of William Alsop are commemorated in our annual Alsop Award for outstanding contributions to the science of leather manufacture or for service to the Association. It was the writer of this note, while serving as President of the Association in 1938, who suggested that the newly established award be so named. Perhaps it may not be out of order now to suggest that the name be changed to the "Alsop-Williams Award".

When the Council undertook the difficult task of selecting a new editor, it soon became apparent that the editor's duties involve two distinct functions, requiring quite different qualifications. The first function is to pass on articles submitted for publication; in this capacity the editor must be a leather chemist. The second function involves all the details of publication, from preparation of the copy for the printer to reading the final proofs; in this capacity the editor ought to have journalistic experience. Dean Williams, ably assisted by Ralph Twining, had performed both functions. It was not difficult to think of several members of the Association who were qualified to direct the general policy of the Journal and select the material to be published, but not one of these men had the time or the strength to take on the whole editorial task in addition to his regular, full-time job. The logical solution seemed to be to divide the editorial duties between an Editor-in-Chief, chosen from the membership, and a Managing Editor.

As Editor-in-Chief the Council selected the writer of this note. As he has been active in the affairs of the Association for some thirty years, and is well known to all members of the Council, it must be assumed that the Council had reason to believe that he is qualified for the position. Let us hope that they were right. At the very least, your new Editor-in-Chief possessed one not unimportant qualification which most other candidates lacked, namely, a willingness to take the job.

As Managing Editor, the Council has employed Professor Earl J. Watt of Lowell Technological Institute, Lowell, Mass. A Harvard graduate (A. B. and A. M. in Romance Philology) and a professional educator for over 20

years, Professor Watt is Coordinator of Special Services at Lowell Tech where his duties include responsibility for publications and public relations.

The Editor-in-Chief will serve for a three-year term, Providence permitting, and will not be eligible for re-election. He will be assisted by the Editorial Board, which will be enlarged and strengthened, and which will play a more active part than heretofore in determining the policies of the Journal. It is the hope of the Council that some member of the new board will be developed as the present editor's successor.

The Editor-in-Chief and the Managing Editor will work together closely to maintain the standards of the Journal, yet, if possible, to make it of greater interest and general usefulness. Any changes will be made gradually, and only after careful consideration. The primary function of the Journal will continue to be the publication of original scientific papers. Your new editors expect to improve and broaden the coverage of the abstract section; to publish, occasionally, full translations of especially noteworthy papers from foreign language journals; and to bring you more news of your Association, including significant items about the professional activities of individual members. In all of this we earnestly invoke your cooperation and assistance, and above all your suggestions.

HENRY B. MERRILL

It is noticeable that most of the attempts to substitute new for old methods of tanning are made by men outside of the trade. Very few of the new inventions, particularly those that contemplate the saving of time, originate within the trade itself . . . There is no topic that requires more vigorous treatment than this, not only for the good of the trade, but for the benefit of that large and unfortunately increasing class of men who desire to get a living by their wits and without labor. As it is now, our Patent Office gives encouragement to this class of parasites, for there seems to be no claim too absurd to receive favor, and patents are multiplied to an extent that no man can keep an account of them . . . What is most needed is at least one Examiner who has practical knowledge of the tanner's art. Such a selection it is not unreasonable to ask, when it is considered that this manufacture (leather) stands second in importance among the industries of the Country.

—*The Leather Manufacture in the United States*, J. S. Schultz, (1876).

The Contribution of Soaking Assistants to Side Leather Quality*

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ABSTRACT

A carefully controlled test, employing 44 matched pairs of sides, was performed to determine the relative effects of sodium polysulfide and sodium hydroxide, used as soaking assistants, on the quality of elk side leather. The use of sodium polysulfide resulted in a slight but statistically significant decrease in the strength of the leather. Possible reasons for this effect are discussed.

INTRODUCTION

Soaking rehydrates the skin protein, partially solubilizes and partially removes the denatured globular proteins, opens up the fibrous structure, and removes salt and surface dirt and filth from the skins or hides. Soaking auxiliary agents are often added to the water to facilitate these operations. Thus, Roddy and Hermoso (5) and Theis and Zable (7) have recommended polysulfides as soaking auxiliaries especially for dry hides. Further, many tanners employ alkaline soaking assistants such as soda ash or caustic soda; such alkaline soaking maintains an increased pH level, so that the growth of microorganisms in the soak water is repressed. Further, current practice has extended the use of polysulfides, originally recommended for the soaking of dried hides, to the soaking of green salted cattle hides.

Though laboratory experimentation and commercial practice suggest the value of soaking assistants, no commercial experiments seem to have been described in the literature which would offer information on the influence of the soaking assistants on the leather quality and properties. Therefore, it was decided to carry out a tannery experiment to evaluate the influence of caustic soda, or sodium hydroxide, and the influence of sodium tetrasulfide upon the quality and properties of the leather produced from such soaking practice. The cooperation of a side leather tanner was available, so that this experiment could be conducted upon a semi-production scale.

*Presented at the Fifty-First Annual Meeting, Swampscott, Mass., May 22-25, 1955.

EXPERIMENTAL PLAN

Forty-five hides were selected in the tannery hide cellar; these hides were taken from four small packer lots coming from Indiana, Missouri, and Mississippi sources. A total of 4,877 hides were included in the original packer lots, which were winter take-up packs. The 45 selected hides were split down the backbone and marked with either a single or double punch to identify the two different packs being made for the two different soaking treatments. The marking and side assignment resulted in each pack containing a side from every hide, with right and left sides alternately going to each soak pack. Further, each side was coded to preserve its identity throughout the tannery processing. This particular side assignment practice was chosen to make the comparison of the two soaking treatments more sensitive, because of the bilateral symmetry of hides with respect to the backbone.

The trimmed sides were individually weighed and then sampled for laboratory examination of the properties of the hides. The sampling location was adjacent to the backbone, and two-sevenths of the distance from the root of the tail to the base of the neck, with the long dimension parallel to the backbone. This sampling location was chosen because Deasy (1) has found that this location is most sensitive to the hide average composition. The specimens were individually weighed, wrapped in water-retaining plastic film and shipped to the Tanners' Council Research Laboratory for analyses.

The 45 sides for the caustic soda soak had an average weight after trimming of 18.9 pounds, with the heaviest side weighing 24.5 pounds and the lightest side weighing 14 pounds. The 45 alternate sides for the polysulfide soak had an average trimmed weight of 18.9 pounds, ranging in weight from 13.7 to 26.1 pounds. For each soak pack sufficient additional sides for normal tannery production of side leather were added to bring the total soak pack weight to 7,000 pounds of trimmed sides. The hides were green fleshed before being put into the soak, following a short drum washing.

Table I shows the soaking characteristics applicable to the two soaking packs. The sodium hydroxide, or caustic soda, soaking was the routine soaking procedure in the tannery where the work was done. Hence, in the discussion to follow, it will often be referred to as the control pack. The data demonstrate that the soaking procedure was typical of customary side leather soaking. The caustic soda soak started at a slightly higher pH, but ended at a lower pH than the tetrasulfide experimental soak pack. Neither soaking auxiliary removed excessive protein from the pack; it is possible that some volatile ammonia was lost from the spent soak liquors during shipment from the tannery to the laboratory for analysis. However, the absence of collagen, as determined by hydroxyproline determination, in the soak liquors is an indication that the sides were not seriously deteriorated prior to or during soaking. Further indication of the hide quality will be found in the hide analytical data given later.

TABLE I
CHARACTERISTICS OF THE SOAKING PROCESS

(7,000 lb. soaked 20 hours in 2,600 gal.; float ratio, 3:1)

		Control Soak	Experimental Soak
Initial soak liquor Composition	Additive in lb.	1.5 technical NaOH	20.6 100% Na_2S_4
	pH	9.3	9.1
Final soak liquor analyses	Temperature	70°F	71°F
	pH	8.5	9.1
	Protein—lb./100 lb. of hide	0.010	0.014
	Collagen	Absent	Absent

The soaked sides were then placed into the tannery's three-day liming process, using sufficient sodium sulfhydrate to permit reclamation of top-quality hair. The unhaired sides were then collected from both soaking treatments, and carried through the remainder of the process together in one lot. The tannage employed was a 24-hour bate-pickle-tan process. Calcium formate was added just prior to the completion of pickling, followed by the chrome liquor on top of the spent pickle liquor. The one-bath chrome-tannage liquor contained 80 pounds of chromic oxide for 4,800 pounds of limed stock weight. Tannage continued for about three hours before starting borax neutralization; total tannage and neutralization time was four hours. After lying in pile for 24 hours, the stock thus tanned will show only two per cent of the sides with a shrinkage temperature below 212° F., with the average value being 220°.

The leather was then wrung, set out, blue sorted, split and shaved, and sent to coloring. The coloring involved a five per cent vegetable extract mordanting, followed by dyeing with acid dyes. After fatliquoring, the leather was pasted, dried, conditioned and staked to proper feel, buffed, and finished to yield a so-called elk leather. In the splitting and staking operations, the plant operation procedures were modified to some extent. The control side of each hide was split to its proper weight; this resulted in eight sides of medium weight, 29 sides of medium-heavy weight, and eight sides of heavy weight. In staking, each control side was staked according to normal crust-sort instructions for staking. On the alternate sides from the experimental polysulfide soaking, the splitting and staking was the same as that used on the control side from the same hide. This was done to avoid the introduction of biasing or masking effects from these operations which would interfere in the tannery evaluation of the leather.

The finished leather was given the customary tannery evaluation for break, firmness and smoothness, or "pasting workmanship". Further, the leather was measured for yield and graded as is customary for elk leather.

The sides of the finished brown leather were sampled in the area to the rear of the hide area sampled in the cured sides. Specimens 4 by 8 inches in size were removed adjacent to the backbone, with the long dimension parallel to the backbone line. Thus, the leather sampling secured kidney area pieces from each of the sides for laboratory evaluation of the leather. The tannery personnel coded these specimens so that their original side source was identifiable, and submitted the coded specimens for laboratory evaluation.

It should be emphasized that during all the evaluations of this leather or the hides from which the leather was made, the sides were coded so that bias in favor of either treatment was impossible. Further, except for the deliberate variation in soaking, every effort was made to keep the tannery processes and the evaluation of the leather identical for all the sides. No selection of the data secured was made, except that one hide was dropped from the experiment entirely because of a splitting error in the tannery. These precautions, coupled with the experimental design, are believed adequate to make the experiment fair and sensitive to any possible effect of the soaking variable.

LABORATORY TECHNIQUES USED TO EVALUATE THE HIDES

When the hide specimens were received in the laboratory, they were immediately fast-frozen and held in this state until they were subjected to testing. The first operation involved the fleshing of the frozen specimens, using a small fixed-knife leather splitter; it was thus possible to flesh the pieces to the usual depth involved in tannery green fleshing. Further, the hair was clipped from the specimens, using the type of clippers used in making hair-on leather. The weight changes in the specimens were followed in these operations; Figure 1 shows that the amount of hair and flesh removed was equal to 22 pounds for every 100 pounds of tared hide. These tared-hide specimens were subjected to chemical and physical testing to secure the data in Table II and Figure 1.

The state of cure of the hide was evaluated by the determination of the volatile nitrogen content, as suggested by Koppenhoefer and Somer (2). It was found that the average value for the hides was 0.31 per cent, based on the total hide nitrogen. In our experience, this level is acceptable for satisfactory cure. Higher values, say 0.35 or greater, usually are found associated with other evidence of poor cure. Further, the tared hides were analyzed for leather-making substance, using the hydroxyproline determination as an indicator of collagen. When these analyses were calculated back to the the hide basis, it will be noted that 32 pounds of leather-making substance was present per 100 pounds of tared hide. Expressed on the original, or tannery hide basis, only one-quarter of the hide weight was found to be leather-

making substance. This is fairly representative of green salted hides when tested by the method described here. Finally, a material balance for the tared hide was determined. These results comprise the bottom bar of the hide composition chart in the upper part of Figure 1. It will be noticed that almost 60 per cent of the tared hide is composed of water and ash, or salt; these are typical analyses for such hides. The fat content is rather low, slightly less than three per cent; many lots of hides we have examined in this fashion run two or three times this level. Also, the total protein content of the hides is 38 pounds, or about 120 per cent of the leather-making substance; again, this is a typical analysis. These figures are recorded to indicate that the hides used were representative of normal well-cured commercial green salted hides.

TABLE II

CHARACTERISTICS OF HIDES USED

Hide Characteristic		Units	Average Value 44 Hides	Hide Variability *Max.*	*Min.*	*Std. dev.*
	Hide weight	Pounds	37.7	49.7	27.7	5.0
	Hair and flesh tare	% of hide wgt.	18.3	26.9	11.2	4.2
Physical properties	Puncture Resistance					
	Thickness	Mils	172.5	215	125	15.5
	Strength	Pounds	170.0	222	108	22.8
	Stitch-Tear Strength					
	Thickness	Mils	164.3	222	126	16.6
	Strength	Pounds	124.9	154	95	14.7
	Tongue-Tear Strength					
	Thickness	Mils	163.6	210	124	13.5
	Strength	Pounds	59.8	82	40	9.1
Material balance (tared hide basis)	Water	%	44.2	47.7	39.5	1.8
	Fat	%	2.8	11.3	0.8	1.92
	Ash	%	14.7	16.4	12.8	0.89
	Protein	%	38.0	40.7	34.2	1.45
	Total	%	99.7	102.0	98.0	0.81
Quality indices (tared hide basis)	Collagen	%	32.1	36.0	27.6	2.2
	Volatile nitrogen	% of total N	0.31	0.36	0.21	0.033
	Histological cure index*		49	59	34	6.1

*A score, varying between 60 for a well-cured hide and 24 for a very poorly cured hide, resulting from the average of three observers' independent microscopic estimations of cure quality.

Data on the mechanical properties of the sides were secured to evaluate their similarity and to furnish evidence for the assumption of bilateral symmetry in physical characteristics in the design of the experiment. These data

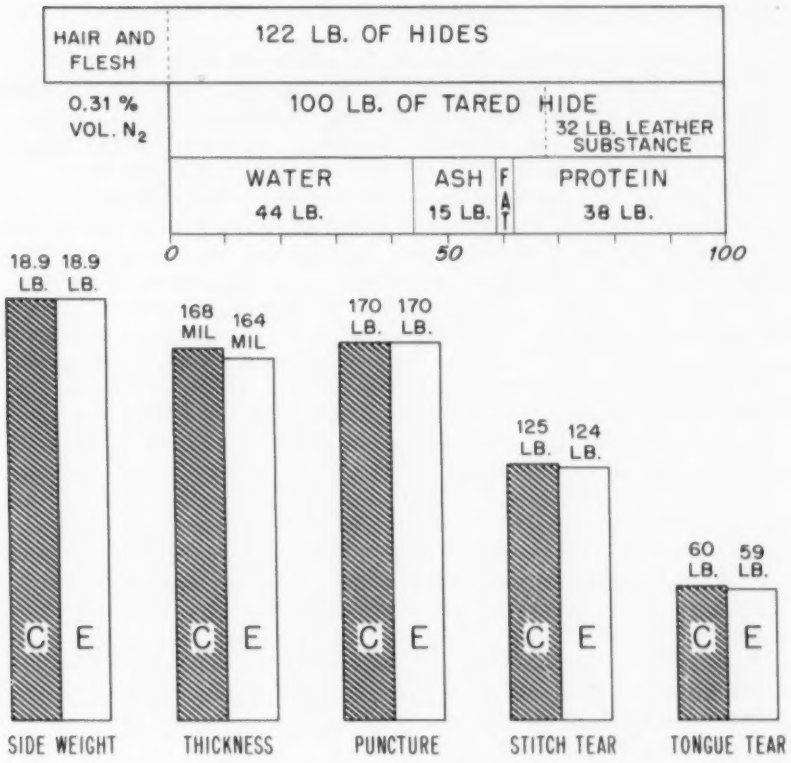

FIGURE 1.—Characteristics of hides used.

comprise the lower half of Figure 1. The identical average weight of the two halves has been previously noted, and is shown first. Second, the average thickness of the tared hides is recorded. The four-mil difference noted is not significant when the errors of measurement as well as fleshing and hair clipping differences are taken into account. Further, the load necessary to force a one-eighth-inch-diameter steel ball through the hide, recorded as puncture resistance, and the stitch-tear and tongue-tear strengths of the hides, as measured on the Scott tensile tester, are also indicative of the fact that the hides show bilateral symmetry. These average differences are too small to be significant when compared to the hide variability observed among the 44 hides.

TECHNIQUES USED TO EVALUATE THE LEATHER PRODUCED

The tannery producing the leather in this experiment made their customary tannery evaluation of leather quality, along with their evaluation of the significance of the results. These data have been integrated with the laboratory evaluation of the leather specimens received to present a thorough picture of the leather resulting from the two different soaking auxiliary agents.

The laboratory evaluation of the leather specimens submitted included the determination of their thickness, the Mullen grain crack value, the Mullen burst strength, the 3/8-inch-diameter ball-puncture resistance, the stitch-tear strength, and the tongue-tear strength. Further, certain non-destructive tests were applied. The hardness of the leather was measured on the Trionic hardness tester, which reports an arbitrary number proportional to the resistance of the leather to the penetration of a small indenting tool. The Instron stress tester was used to secure data relative to the forces involved in the stressing of the leather to loads well below that required to rupture the leather, and more comparable to the stress-strain realm which might be met in the use of the leather. This was a cyclic test, involving three successive extensions of the leather to a 15 per cent extension, followed by immediate unloading. This extension and relaxation took place at a rate of one-half inch per minute; since a one-inch specimen length was used, each extension and relaxation required 18 seconds. Data were secured on all three cycles, but it was found that the data from the first cycle were sufficiently representative for our purpose. Hence, data are presented on the load necessary to secure 15 per cent extension, an arbitrary estimate of the work lost as heat and fiber damage in the first extension and relaxation of the specimen, and the proportion of the extension which was regained at the end of the 18-second relaxation period.

The leather specimens were individually submitted to complete chemical analysis for moisture, ash, chromic oxide, hide substance or protein, and grease. Further, a material balance for the leather was calculated by the method of Kubelka (3), which assumes that the chrome-tanning salt may be calculated from the chromic oxide content by multiplication by 2.71. It may be recorded at this point that it has been our experience that this empirical factor permits the determination of a reasonable material balance on chrome-tanned leathers, and that it is valuable as an overall check on the validity of the analyses.

DISCUSSION OF THE RESULTS SECURED

Figure 2, Table III, and Table III-A show the tannery grading report on the leather from the 44 control, or caustic-soda-soaked, sides, and the 44 experimental, or polysulfide-soaked, sides. This grading report does not indicate any significant effect due to the soaking; it is not surprising that this

is true, since grading primarily reflects factors such as potential cutting value which soaking will influence very little.

Figure 2 and Table III also show the average chemical composition of the specimens received. The average analysis is similar for both soak packs. The experimental soak pack contains slightly less protein, and slightly more grease, chrome-tanning salt and residual organic matter. In each case, the level of the residual organic matter is about five per cent, which is consistent with the level of retannage and the amount of dye used on the leather. It may not be wise to attach too much significance to these differences in analysis, although they are the averages of 44 separate analyses in each case, and hence have far more validity than the usual chemical analysis which is the average of two analyses upon a composite sample. At this point we merely note the lower protein content of the experimental leather.

Table III and Figure 3 present the data on the physical properties of the leather. The top of Figure 3 presents the data secured from the conventional breaking tests where the leather is ruptured in one application of force. It will be noted in each case that the experimentally soaked hides have yielded weaker leather than the caustic soda, or control, soaked sides. While these differences are not large, the sensitivity of this experimental design is such that the possibility of their occurrence due to pure chance is less than 1 in 10 for the Mullen grain crack and Mullen burst, and less than 1 in 100 for ball puncture, stitch tear and tongue tear. It may seem that these differences are not of practical importance; however, when we combine these average values with the estimates of hide variability secured in the experiment, we get a better picture of the significance of the results. Thus, for grain crack, which is judged to reflect possible problems in lasting, we can calculate that one-sixth of all the leather produced in the experimental procedure would crack below 200 pounds; while the same fraction defective would be reached at 250 pounds with the caustic-soda-soaked pack. Since this region of grain-crack resistance is very significant, it seems evident that practical significance may exist for these relatively small differences. Equivalent service evaluation is not available for the other tests. However, the principle just illustrated is still valid; the leather from the experimental soak will show a higher level of defective leather at any particular performance level we might find desirable.

The lower strength of the leather from the experimental soak may reflect to some extent the fact that it is on the average thinner, even though the splitting was controlled to give the same thickness to each side from the same hide. However, as we shall see later, the effect of thickness on strength characteristics has been overemphasized.

The non-destructive tests similarly present data which show that the experimental leather is different from the leather from the tannery caustic-soda soaking. First, the experimental leather is softer to the Trionic hardness

TABLE III

CHARACTERISTICS OF THE LEATHER PRODUCED

Leather Characteristic	Units	Regular Soak—44 Sides Average Value	Side Variability Max.	Min.	Std. dev.	Polysulfide soak—44 Sides Average Value	Side Variability Max.	Min.	Std. Dev.
Water	Weight loss—100°C.—%	13.0	14.5	11.4	0.88	13.0	14.3	11.6	0.75
Grease	$CHCl_3$ extract—%	6.3	8.59	4.45	1.11	6.4	8.37	4.13	0.98
Protein	% N_2 x 5.62	64.8	69.0	60.6	1.97	64.4	68.6	59.4	2.05
Chrome salt	% Cr_2O_3 x 2.71	7.9	8.83	6.59	0.46	8.0	8.73	6.75	0.44
Excess ash	% total ash—% Cr_2O_3	2.6	3.50	1.69	0.46	2.7	3.78	1.69	0.44
Material balance	Sum of above 5	94.7	97.0	91.6	1.36	94.5	97.3	91.1	1.48
Chromic oxide	% Cr_2O_3—as is basis	2.92	3.22	2.43	0.17	2.96	3.22	2.49	0.15
Chromic oxide	% Cr_2O_3—H. S. basis	4.51				4.57			
Mullen strength	Thickness—mils	72	85	61	6.12	70	88	61	6.86
	Grain crack—lb.	348	575	135	105	328	675	130	117
	Burst strength—lb.	466	690	160	142	435	737	135	142
Puncture resistance	Thickness—mils	76	91	65	6.44	73	92	59	7.02
	Pounds	42	65	7	15.1	36	63	11	12.2
Stitch tear	Thickness—mils	76	92	63	6.75	74	99	61	7.42
	Pounds to tear	60	89	43	10.7	52	78	9	14.4
Tongue tear	Thickness—mils	72	86	61	6.40	70	87	57	6.71
	Pounds to tear	16	22	8	4.1	14	22	5	3.6
Yield	ft./lb.	0.89	1.05	0.75	0.079	0.89	1.08	0.69	0.086

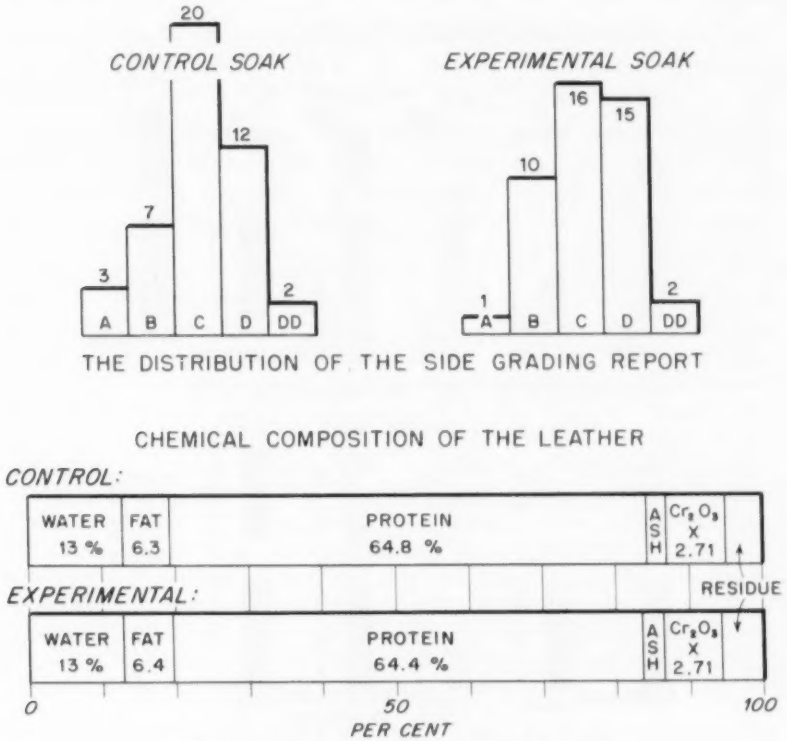

FIGURE 2.—Characteristics of the leather produced.

TABLE III-A

TANNERY EVALUATION

	Regular Soak	Polysulfide Soak
Temper	Standard	Firmer
Break	Equivalent	Equivalent
Grading	Equivalent	Equivalent
Side distribution	3, A; 7, B; 20, C; 12, D; 2, DD.	1, A; 10, B; 15, C; 16, D; 2, DD.

test; it is easier for the leather to be penetrated by the small point of the tester. Second, the polysulfide-soaked sides have yielded leather that requires less load to extend it by 15 per cent; further, during this extension and relaxation, less work is required by the polysulfide-soaked stock, and the

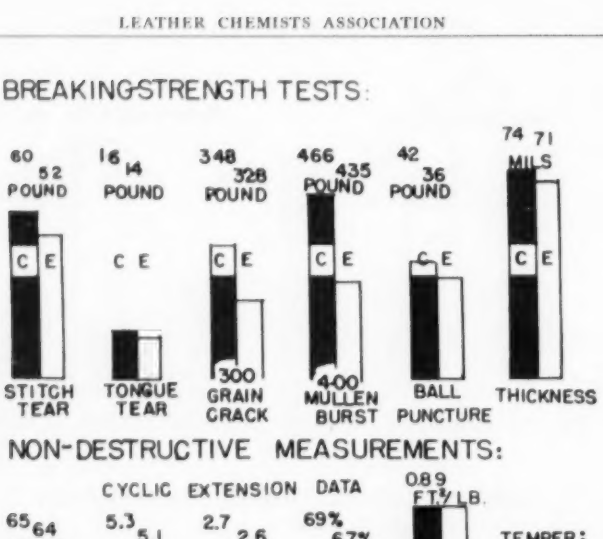

FIGURE 3.—Physical properties of the leather.

TABLE IV

CORRELATION BETWEEN THE LEATHER PROPERTIES

(Control and Experimental Side Correlation Averaged)

Physical Property	Thickness Mils.	Protein %	Fat %
Grain crack	+0.02	+0.51	—0.44
Mullen burst	+0.21	+0.63	—0.56
Ball puncture	+0.29	+0.59	—0.43
Stitch tear	+0.31	+0.49	—0.31
Tongue tear	+0.38	+0.41	—0.58

5 % level of significance : 0.296 r
1 % level of significance : 0.383 r

extension is less elastic. This is true even though the tannery was unable to detect any difference in the yield of the leather or its break, although it was judged that the experimental leather was firmer in temper.

Table IV presents some data which will aid us in our interpretation of these results. Since each leather specimen had been individually subjected to chemical analysis and physical testing, it was possible to examine the data secured for factors which might contribute to the strength of the individual specimen. It commonly is assumed that the thickness of the specimen contributes materially to the variability of the physical strength values secured. It is customary to divide the load value by the thickness, thus assuming a linear relationship between breaking load and thickness. However, this assumption is questionable, and Mitton (4) has shown that the assumption is not valid. It seemed to us that the amount of protein fibers in the leather and the amount of fat on the leather fibers would influence the leather strength. It was therefore decided to use the statistical technique for the determination of the correlation coefficients to secure some measure of the influence of leather thickness, protein, content, and fat upon the strength of the leather. Correlation coefficients vary between -1 and +1, the extreme values indicating perfect correlation so that the relationship between the two factors can be expressed as a straight line. As the correlation coefficient approaches zero from either direction, an increasingly random relationship exists between the two factors. Positive correlation occurs when the two factors increase simultaneously, and negative correlation occurs when one factor is increasing in value while the other factor is decreasing in value.

The values secured from the leather produced from the control-soaked skins and the polysulfide-soaked skins were used separately to calculate correlation coefficients. Then the two separate estimates were combined to give better estimates of the true correlation coefficients between the strength values and the thickness, protein, and fat content by the use of the Z-weighting technique (6). The correlation coefficients thus calculated are given in Table IV. It will be noted that there is a positive correlation coefficient for all the physical properties and the leather thickness and its protein content, and a negative correlation coefficient between all the physical properties and the fat content of the leather. Further, it will be noted that the correlations secured for the effect of thickness are the smallest in value, and reach a five per cent significant level only for the two tear-strength methods. On the other hand, the correlations secured from protein and fat are all significant values. Moreover, the expected positive correlation between the leather strength and its protein content has been secured. It may seem that the correlation between strength and fat should not be negative. However, it must be remembered that the average fat content of these leathers is 6.3 per cent, and that it is generally expected that high fat levels cause weaker

leather on commercial, staked leather. We have also found this same negative correlation from another commercial leather in a similar experiment. It is also certainly logical that excessive lubrication will cause the fibers to slip over one another more readily, so that leather strength would be decreased. Further, there is a very strong negative correlation between the fat content of the leather and its protein content. In other words, at high fat levels the fat merely dilutes the fibers which after all must establish the strength of the leather.

In retrospect, as we look at all the results, it seems worthwhile to attempt to develop a coherent postulate for all the results secured. The action of polysulfides on the skin in soaking is probably that of solubilization and removal of greater quantities of the globular proteins, or cementing substance, from the skin or hide. This results in a hide which is somewhat more readily penetrated by the chrome-tanning material, the vegetable-tanning material used in mordanting, and the fatliquoring oils, resulting in a finished side which is slightly poorer in protein than the side given the alkaline soak. When the sides containing slightly less protein are split to weight, a lesser thickness results. When the sides with the greater fiber separation resulting from the polysulfide soak are staked, they are further loosened up resulting in fewer fiber adhesions and accordingly less strength but softer leather. Futhermore, this hypothesis is consistent with the observations that the control-soaked hides with more protein and thickness require more force to extend them, and liberate more heat in extension. The greater number of fiber adhesions would require this, but would also produce a more resilient fabric, which the extension recovery data indicate. The only inconsistent information available is the fact that the tannery personnel judged the polysulfide-soaked leather to be firmer in temper. It may be noted, however, than one grader was unable to detect a difference, even though two others did agree that the polysulfide-soaked leather was firmer in temper.

SUMMARY

1. A tannery experiment on the effect of a caustic soda and a polysulfide soak has been extensively evaluated by tannery and laboratory methods.

2. The results indicate that the polysulfide soak on the green salted hides used has produced a slightly, but significantly, weaker elk side leather.

3. This may result from a greater degree of fiber separation and from the removal of the globular proteins, or cementing substances, so that the fiber adhesions which contribute to the leather strength are reduced to a greater extent, and also from the lower level of protein content in the thinner leather resulting from the polysulfide-soaked sides.

ACKNOWLEDGMENT

The conclusions drawn in this paper are the responsibility of the authors, but the paper would not have been possible without the excellent cooperation of personnel of the Fred Rueping Leather Company and those of the Tanners' Council Research Laboratory. The extensive work necessary to secure the data on which the conclusions are based is gratefully acknowledged by the authors.

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Received February 3, 1956.

DISCUSSION

MR. AUGUST BOSS (Howes Leather Company): First I want to thank Dr. Lollar for his presentation of an excellent paper, and especially because the paper is not only scientific but also practical enough to help all of us fellows in the tannery.

MR. LEO RIESE (Beggs & Cobb, Inc.): I would like to ask Dr. Lollar where he obtained his samples for testing—what sections of the hide were used?

DR. LOLLAR: All examination of the leather for chemical, physical and other histological data which we did not report here was made on approximately four by eight inch blocks taken adjacent, but slightly below, the backbone line in the kidney area of the side. It was slightly in front of the area which has proven to be very sensitive to the average of hide leather quality and adjacent to the sampling area in the hides, which was selected because our experimental results, secured by Dr. Deasy, proved that the hide sampling area was the most sensitive to reflect hide average quality.

We made an attempt, in other words, to reflect hide average quality in our sampling locations.

MR. THOMAS BILLINGTON (Beggs & Cobb, Inc.): Dr. Lollar, when you speak of bilateral sampling, do you mean essentially running a siding experiment—comparing alternate rights with lefts?

DR. LOLLAR: That is correct. Each pack for the control and experiment contained an alternate side from the same hide. Each pack for the control and the experiment contained nearly an equivalent number of rights and lefts by an alternate procedure.

MR. C. DAVID WILSON (Fred Rueping Leather Co.): Although Dr. Lollar has been speaking of averages, in his paper he mentioned the coding of each side. The identity of each side was still available so that the two sides of the same animal could be observed at the end of the experiment.

DR. LOLLAR: In a paper which will follow, some comparisons between hide and leather properties will be made. It was essential in this experiment that a coded identity of sides be maintained throughout. The sensitivity of the experiment would have been considerably decreased if that technique had not been followed.

MR. BILLINGTON: In order to apply statistical analysis in your work, what is the minimum number of hides or matched sides you would have to work with?

DR. LOLLAR: The minimum number is dependent on the magnitude of the difference which you wish to detect. On the basis of information available to us when the experiment was planned, I told Dave Wilson that I wanted forty hides. He chose forty-five, so we would have enough if we lost any. We lost one. We eliminated nothing else. We therefore ended up with forty-four.

We could have run as many as a hundred. We could not have detected much if we had had many less than we had. But you cannot answer the question categorically. You have to have some estimate of how much error you are going to have and how small a difference you wish to detect.

MR. BILLINGTON: In line with that question, when you were talking about confidence limits, you used 99 and 95 per cent.

DR. LOLLAR: That is correct.

MR. BILLINGTON: Would you generally recommend using a confidence limit less than 95 per cent as safe?

DR. LOLLAR; Again it is a decision to be made; a statistical method does not relieve the investigator from the necessity of using a common sense approach to the results. I am not an arbitrary 95 per cent confidence-level tester. I made some reference to one in ten. It all goes together in my total picture. If I had to be pinned down to a level, I would be a 95 per cent level tester.

MR. BILLINGTON: One further question: when you were comparing numerical data of sample A with B, were you using straight numerical averages there, or standard deviations, or what?

DR. LOLLAR: I don't understand which data you are referring to.

MR. BILLINGTON: Say the Mullen data. When you compared A with B, was that straight numerical average data?

DR. LOLLAR: We made the assumption of bilateral symmetry which I indicated was proven for the hide characteristics, so on the leather the paired deviates "T" test was used to check the differences.

A similar, though not quite as sensitive conclusion, would be drawn if we had used the normal "T" test or an analysis of variance technique, but the particular conclusions that were stated were based on the paired deviates "T" test. It is the most sensitive test we could have used. We did assume bilateral symmetry, but we believe it is demonstrated.

DR. ROBERT STUBBINGS (Lehigh University): Dr. Lollar, I noticed that there appeared to be a distinctly opposite result from the Instron and stretch data in terms of firmness of leather to that obtained by tannery evaluation of temper. It seemed that the tannery found the experimental leather to be firmer, whereas the mechanical testing showed the control leather to be somewhat firmer. Would you like to comment on the reasons for this?

DR. LOLLAR: You are right. There is an apparent contradiction there. It certainly suggests additional problems for study.

I might point out, however, that it is my feeling that tannery evaluation of firmness primarily results from a flexing evaluation of the leather. Is that not right?

MR. WILSON: Yes.

DR. LOLLAR: That involves a flexural characteristic of the fibers which may not have been measured in the tensile elongation of the leather which was involved in the Instron data. Having gotten the apparent contradiction, I will have to do some more Instron work to see whether the temper reflects other properties than those I have reported here.

DR. STUBBINGS: I wonder, in the course of your mechanical testing, whether you did any flexural testing?

DR. LOLLAR: No, that has not been done. There is sufficient leather available so that I think I will do some more work on this. I would say that in connection with fatliquoring data which Mr. Roddy is reporting this afternoon, we have used more tests and in general my expectation would be

that the test would go somewhat in the same direction, but they certainly differ in sensitivity to detect differences. We are just beginning to get into the whole new field of what are the properties that determine the feel of leather, and I am certain it is not the breaking strength of leather.

We have got to understand these cyclic properties of leather. Today I do not. It is going to be something I will do a lot of work on in the next few months.

DR. STUBBINGS: I think all of us are very interested in the possibilities of testing leather for those qualities which manufacturers buy it for. This is the start of that sort of thing. Consequently I was extremely happy to see it presented today.

In 1955, the U. S. shoe industry established an all time productivity or man-hour output record of 1.34 pairs, or an annual average of 2,589 pairs per production worker. This is the highest level of man-hour, or annual pairage output per worker ever reached in the history of shoemaking. It is estimated that this level is approximately 35 per cent greater than that of the next closest nation.

The Economics Research Division of the Boot and Shoe Workers' Union, AFL-CIO, which released its important, 'Shoe Industry Productivity Report,' states that, 'the U. S. shoe industry, perhaps without fully realizing it, has over the years been showing one of the best production climbs in the entire manufacturing field.'

In 1955, the shoe industry's man-hour output rate was 5.5 per cent above 1954; it was 17 per cent above 1949; it was 34 per cent over 1939, and more than 100 per cent above 1925.

—*Weekly Bulletin of Leather and Shoe News*, March 10, 1956.

In the sale of unsalted green hides, there are certain reprehensible frauds which it is difficult to provide against. For instance, not only are the horns, ears, and other less valuable parts left upon the skin, but the butcher, in order still further to increase its weight, beds the animal, before slaughtering it, in filth and mire, and then, after skinning it, trails the hide upon the dusty ground.

—*Arts of Tanning and Currying*, Morfit, (1852).

A Paper Chromatographic Analysis for Collagen and Collagen Derivatives*

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ABSTRACT

Collagen was completely hydrolyzed with hydrochloric acid. After this treatment, 18 amino acids were quantitatively separated from the hydrolysate by two-dimensional paper chromatography. The paper (Whatman No. 1) was irrigated in one direction with a mixture of methyl alcohol, pyridine, and water, and in the other, with mixed tertiary butanol, methyl ethyl ketone, diethylamine, and water. Residual diethylamine was removed from the paper by steam distillation at approximately 75°C. The spots of individual amino acids were revealed by the color produced when treated with ninhydrin. They were cut out, after which each colored amino acid derivative was dissolved and its optical density determined with a spectrophotometer. The analysis of collagen agrees well with the generally accepted literature data. Specific colorimetric tests for tyrosine, phenylalanine, and hydroxyproline were used to obtain comparative data for these amino acids.

INTRODUCTION

Since the classical paper by Consden, Gordon, and Martin (1) in 1944 on the analysis of protein hydrolysates by two-dimensional paper chromatography using the system collidine-phenol plus ammonia (coal gas), a variety of other solvent combinations have been employed for this purpose (2). In this paper a quantitative, two-dimensional paper chromatographic procedure is described which was adapted primarily from a qualitative method initially introduced by Redfield (3). The method is simple and requires for accurate analysis of collagen hydrolysate, aliquots containing as little as 150 micrograms of protein. The data are reproducible providing the necessary precautions are observed.

Although complete analysis of collagen has been attained by others (4), the chromatographic method permits accurate analysis of collagen or its derivatives relatively quickly and without elaborate equipment. The method provides separation of essentially all the amino acids. Leucine and isoleucine are segregated from the other amino acids but not from each other. The same is true of hydroxylysine and lysine. The method should provide a useful tool for a study of collagen degradation and structure.

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MATERIALS

A pure grade of collagen was obtained by splitting off the epidermal and fatty layers of a partially dehydrated steer hide procured within an hour after the animal's death. The corium was dehydrated with acetone, dried at room temperature, and ground in a Wiley mill to pass a ¼-inch sieve. The collagen powder was then extracted repeatedly with a 10-per cent solution of sodium chloride until protein matter had ceased to dissolve. Thorough washing with tap water and finally with distilled water followed. Fatty materials were removed by a series of alcohol and acetone extractions at room temperature. The collagen was dried in air and again ground in a Wiley mill to pass a 4-mm. sieve.

METHODS

Paper chromatographic method

1. *Development of the chromatogram*

In preparation for chromatographic separation, collagen was hydrolyzed with constant boiling hydrochloric acid (previously distilled from an all-glass unit) in sealed glass tubes at 112°–115° C. for 17 hours. The hydrolysate was removed from the tube and filtered. The concentration of hydrolyzed collagen was computed from a determination of nitrogen in the filtrate.

Completeness of hydrolysis was ascertained by comparing the amino nitrogen /total nitrogen ratio of the hydrolysate with that of a synthetic amino acid mixture (Table II) whose composition paralleled that found in the collagen hydrolysate. The α amino nitrogen was determined by the formal titration method and the Van Slyke manometric procedure.

Ascending chromatography was employed throughout. Flat-bottomed glass cylinders (6 inches in diameter and 12 inches high) were used as chromatographic chambers. Crystallizing dishes 2½ inches in depth, ground to give a close fit with the lip of the glass cylinder, served as lids. A rubber electrical tape provided an air-tight seal between lid and chamber.

Sheets of Whatman No. 1 paper were cut 36.5 cm. by 37 cm. and a small (4-mm. diameter) penciled spot was placed 6 cm. from the bottom in the 36.5-cm. direction and 4.5 cm. from the vertical edge. A microaliquot (4-14 μl.) of the hydrolysate or of a standard solution containing the amino acids was transferred by means of a micropipet to the small penciled spot. The spot was kept discreetly small by drying the spot after each application of less than one microliter of solution. Usually the equivalent of 150–190 micrograms of protein was transferred to the spot. The sheet was then stapled in the form of a cylinder in preparation for the first dimensional run.

The solvent systems suggested by Redfield (3) in his qualitative work have been employed. In the first direction a mixture of methanol, water, and pyridine (20:5:1) was used. Forty-eight ml. of solvent mixture was used in the

first direction which required 8 to 8½ hours for completion. After 15 minutes of drying in a well ventilated hood, the staples were removed from the paper cylinder and the sheet restapled so that irrigation with the second solvent mixture would occur at right angles to that of the first. The second solvent mixture consisted of tertiary butyl alcohol, methyl ethyl ketone, water, and diethylamine (10:10:5:1). With 48 ml. of this solvent mixture, usually 21 to 23 hours were required for the solvent front to reach the top of the paper. Care was always taken to remove the sheets as soon as possible after either solvent front had migrated to the top. During development in either direction the chromatographic chambers were kept in a constant-temperature room.

Some time after the present technique had been perfected, Wellington (5) reported a paper chromatographic separation of amino acids on Whatman No. 1 paper. She used Redfield's first solvent mixture but substituted ammonia for diethylamine in the second solvent mixture. This method does not separate the basic amino acids.

After removal from the second solvent, the sheets were dried at room temperature in a well ventilated hood for at least 15 hours. They were then suspended for seven minutes in a clean steam hood into which sufficient steam was introduced to maintain a temperature of 74°–76° C. The steaming procedure was required to remove traces of adsorbed diethylamine from the chromatograms. Failure to remove the adsorbed amine leaves the chromatograms too basic for good color development of amino acids and results in a strong blue background color which gives such high and variable blank values as to make quantitative work impractical.

Redfield (3) has also reported the necessity of removing the amine and he used an autoclave for this purpose. The use of an autoclave in this investigation was not satisfactory. The amino acids were rendered partially inactive to ninhydrin. Fowden and Penny (6, 7) found that, on heating chromatograms in an oven at 90°–100° C. in order to drive off phenol, reduced color yields were obtained on spraying with ninhydrin. The data of Table 1 show

TABLE I

EFFECT OF STEAM TREATMENT ON AMINO ACIDS

Amino Acid	Steamed	Not Steamed
	Optical Density at 570 μ*	
Glutamic acid	433	439
Glycine	498	494
Arginine	209	220
Alanine	540	500
Serine	123	112

*These values determined from uni-dimensional chromatograms using the tertiary butyl alcohol-methyl ethyl ketone-water solvent mixture without diethylamine. The optical densities are the average of three determinations.

that heating the chromatographed amino acids in the steam hood at 74°–76° C. did not reduce their color response. That these conditions were sufficient to remove adsorbed amine from the two-dimensional chromatograms was evident from the absence of any blue background after they had been sprayed with ninhydrin and the color allowed to develop.

Several unsuccessful attempts were made to remove the adsorbed amine by washing the chromatograms with organic solvents or solvent mixtures such as chloroform, petroleum ether, ethyl ether, and a 1:1 acetone-ethyl ether mixture.

2. *Quantitative estimation of amino acids*

The steamed chromatograms were dried and sprayed with a two per cent solution of ninhydrin in absolute alcohol. Wellington (8) has shown the importance of using a sufficiently concentrated solution. An all-glass spray unit was used and care was taken to spray each sheet evenly. To prevent undesirable finger prints on the papers, cotton gloves were used. The sprayed sheets were dried at room temperature for five minutes and then transferred to a chamber controlled at 25° C. and 37 per cent relative humidity. Wellington (9) reported that there is only a narrow range of humidity (35-40 per cent) within which maximum color development for most amino acids can be expected. Thompson *et al.* (10) showed that a constant temperature was necessary for reproducible results and took the further precaution to develop the color in an atmosphere of ethyl alcohol and carbon dioxide. In the present study when color development was allowed to proceed at 25° C. and 37 per cent relative humidity, maximum reproducible color yields of the amino acids (aspartic acid gives a reduced color yield) were obtained in 22-24 hours. Variation of color response was no greater between chromatograms sprayed on different days than within sheets sprayed on the same day. For this reason, once the standard curves had been obtained for each amino acid, it was necessary only to redetermine them intermittently as a check on the procedure.

After color development was complete, the amino acid spots were cut out (along with blank spots selected from four different areas of the sheet), cut into strips, and transferred to test tubes. For those amino acids present in collagen in small amounts, and for the amino acids proline and hydroxyproline, the spot and the blank closest to it were weighed and the fraction of the blank that was applicable thus determined. For the remaining amino acids the total blank correction of the nearest blank was applied. Five ml. of a 50-per cent aqueous *n*-propanol solution were added and the tubes were mildly agitated for 10 minutes. Lint in the tubes was permitted to settle out during 15 minutes. The optical density of the solutions was read with a Beckman spectrophotometer set at 570 μ except for proline and hydroxyproline which were read at 350 μ (8).

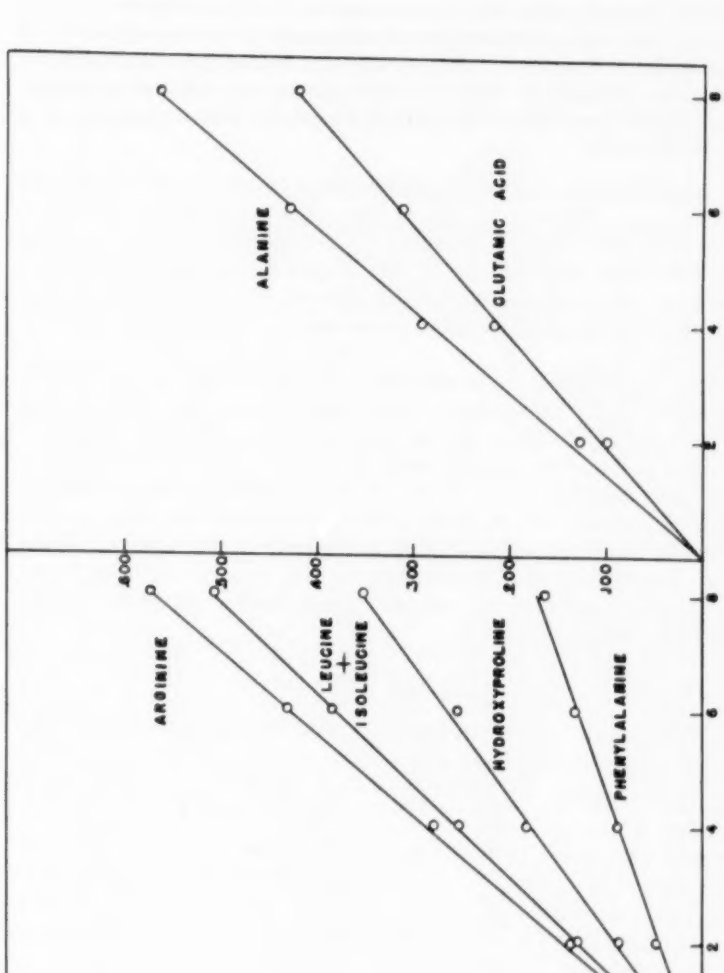

FIGURE 1.—Standard optical density plots for ninhydrin derivatives of various amino acids.

Standard curves of optical density vs. concentration were prepared for each amino acid from data obtained on two-dimensional chromatograms of a synthetic amino acid mixture. Typical examples of these plots are shown in Figure 1. The composition of the synthetic amino acid solution is given in Table II. This composition was selected to parallel that anticipated in a collagen hydrolysate.

Specific colorimetric tests for tyrosine phenylalanine and hydroxyproline. As an additional check on the values obtained by the chromatographic method, three of the amino acids were determined by applying specific colorimetric tests directly to the collagen hydrolysate. The amino acids tyrosine, phenylalanine, and hydroxyproline were determined in this manner since there has been some controversy in recent years regarding their determination.

Tyrosine was estimated by Bernhardt's (11) modification of the Millon-Weiss method (12). Phenylalanine was determined by the Block-Bolling method (12) and by the Hess-Sullivan procedure (13). The latter procedure was modified in that after nitration and subsequent reduction of the dinitrophenylalanine and prior to reaction with 1,2-naphthoquinone-4-sodium sulfonate, the solution was adjusted carefully to a pH of 3.5. Only by this procedure can the maximum color yield be obtained in this specific reaction (14). Hydroxyproline was determined by the original Neuman-Logan method (15) after attempts to use the Martin-Axelrod modification (16) failed to give satisfactory results.

TABLE II

CONCENTRATION OF SYNTHETIC AMINO ACID SOLUTION

Amino Acid	μg./μl.	Amino Acid	μg./μl.
Alanine	1.900	Leucine	0.648
Arginine	1.533	Lysine	0.856
Aspartic acid	1.200	Methionine	0.190
Glutamic acid	2.198	Phenylalanine	0.922
Glycine	5.233	Proline	3.500
Histidine	0.226	Serine	0.666
Hydroxylysine	0.167	Threonine	0.494
Hydroxyproline	2.180	Tyrosine	0.266
Isoleucine	0.404	Valine	0.658

RESULTS AND DISCUSSION

In Table III is shown the amino acid composition of collagen as determined by the chromatographic procedure described in this paper. The data were compiled from the results of four collagen hydrolysates chromatographed in triplicate. An analysis of variance was carried out on the 12 measurements

for each amino acid to determine whether the results varied significantly between hydrolysates. Replicate determinations on different hydrolysates varied no more than replicate determinations on the same hydrolysate. Therefore, the 12 measurements for each amino acid were considered to belong to a single statistical population and the data were treated accordingly.

TABLE III

AMINO ACID COMPOSITION OF COLLAGEN

Amino Acid	Amino Acid per 100 Grams Protein	Standard Deviation*	Standard Error	Standard Error as % of Mean	Nitrogen as % protein N†	Literature Values‡
	g.	g.	g.			g.
Arginine	8.94	0.37	0.11	1.2	15.8	8.59(18), 8.8(4), 8.7(19), 9.0(20)
Lysine + Hydroxylysine	4.92	0.25	0.07	1.5	5.2	5.8(4), 5.4(19), 5.4(20)
Histidine	0.83	0.07	0.02	2.6	1.2	0.8(4), 0.8(19), 0.8(20)
Aspartic acid	6.58	0.46	0.13	2.0	3.8	6.3(4), 6.0(19), 6.0(20)
Glutamic acid	11.3	0.71	0.21	1.9	5.9	11.3(4), 11.6(19), 11.9(20)
Glycine	26.1	1.14	0.33	1.3	26.8	26.2(27), 25.5(24)
Alanine	10.1	0.48	0.14	1.4	8.7	9.5(4), [10.5(22)]
Leucine + Isoleucine	5.61	0.66	0.19	3.4	3.3	5.6(4), [6.7(22)]
Valine	2.98	0.26	0.07	2.4	2.0	3.4(4), [2.75(25)]
Phenylalanine	2.90	0.34	0.09	3.2	1.3	2.5(18), 4.2(4), [2.6(13)], [2.6(28)]
Threonine	2.46	0.27	0.08	3.1	1.6	[2.0(25)], 2.4(4)
Serine	3.76	0.20	0.06	1.6	2.8	3.37(4), 3.76(21)
Tyrosine	1.09	0.13	0.04	3.6	0.5	1.0(18), 1.4(4), 1.0(29)
Methionine	1.0	0.11	0.04	4.0	0.5	0.8(4), [0.8(23)], [1.1(26)]
Hydroxyproline	12.4	0.84	0.24	1.9	7.3	14.0(27), 13.2(15), [12.8(30)], 12.2(31)
Proline	14.8	0.92	0.27	1.8	9.9	15.1(18), 14.6(22), 17.4(27)
TOTAL	115.8				96.6	

*Standard deviation of a single chromatogram.

†18.15 per cent nitrogen in hide collagen analyzed.

‡All values are recorded as grams amino acid per 100 grams protein. Values determined by other than chromatographic methods are underlined. Those determined on gelatin are enclosed in brackets.

Data reproducibility is very good; the standard errors expressed as a per cent of the mean were less than four per cent. The reproducibility of the proline and hydroxyproline values is considered good since these amino acids do not give a strong color response with ninhydrin and their blank values are undesirably high. The separation of proline from tryrosine and of proline and hydroxyproline from alanine is not clear cut. A more accurate analysis of proline and hydroxyproline can be obtained by determining these amino acids on chromatograms on which neither tyrosine nor alanine is estimated. This is because inclusion of small amounts of blue color from the ninhydrin reaction product of either alanine or tyrosine with the yellow proline and orange hydroxyproline excised spots does not introduce serious error. The optical densities of the ninhydrin reaction products of the latter two amino acids were measured at 350 μ where the optical density of the blue reaction products of alanine and tyrosine is near a minimum. The color response of proline and hydroxyproline with ninhydrin is very sensitive to changes in pH. Steaming of the chromatograms may have helped to reduce the variation in residual alkalinity from sheet to sheet.

Collagen is known to contain low concentration of tyrosine, methionine, and histidine. To increase precision, separate chromatograms for these amino acids were prepared with higher amounts of hydrolysate.

As can be seen from Table III, the amino acid values for collagen determined by the method described in this paper agree well with those reported by other investigators. The value obtained for the combination of lysine and hydroxylysine is approximately 10 per cent lower than that obtained with an aluminum oxide column earlier in this laboratory (20) and by other workers (4, 19). No reason can be advanced for this discrepancy. Attempts are being made to develop a paper chromatographic procedure which would permit separate estimations of hydroxylysine and lysine.

TABLE IV

RESULTS OF SPECIFIC COLORIMETRIC TESTS ON COLLAGEN HYDROLYSATES

Amino Acid	Nitrogen as % Protein N	Amino Acid per 100 Grams Protein	Standard Deviation*	Reference to Test Applied
		g.	g.	
Tyrosine	0.43	1.00	0.10	(11)
Phenylalanine	1.23	2.63	0.27	(13)
	1.16	2.49	0.22	(12)
Hydroxyproline	7.78	13.22	0.28	(15)

*Calculated on the data expressed in g./100 g.

Addition of 3.3 per cent nitrogen as amide nitrogen (17) to the sixth column of data in Table III would increase the nitrogen of collagen accounted for to 99.9 per cent.

The present method is of value because a complete analysis may be made of all the amino acids by applying the same technique to them simultaneously. If eight chromatograms are run per sample, quantitative information regarding all the amino acids can be obtained in four to five days.

The data obtained by applying specific colorimetric tests to the collagen hydrolysate are compiled in Table IV. The results are in good agreement with those obtained by the paper chromatographic procedure and provide added confidence in the determination of these amino acids by the paper chromatographic method.

CONCLUSION

A paper chromatographic method has been described which permits one to obtain accurate, reproducible quantitative data on all the amino acids of collagen. The amino acids are separated on paper by a two-dimensional procedure and, after a required steaming treatment, reacted with ninhydrin. The colors produced with ninhydrin are allowed to develop under controlled conditions of temperature and humidity. The color is eluted with solvent and the concentrations of the amino acids are determined by optical density measurements. The amino acid values obtained agree well with those previously reported (see Table III). As a check on the accuracy of the method for the amino acids, tyrosine, phenylalanine, and hydroxyproline, specific colorimetric tests were run for these amino acids on collagen hydrolysates. The results obtained were in excellent agreement with those found chromatographically. The method should be of value in studies related to structure and degradation of collagen and collagen derivatives.

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DISCUSSION

MR. RODDY: In beginning the discussion on paper chromatographic analysis, let us first consider what has been accomplished in the way of technique. The simplification of complicated technique is always welcomed, not only by people in research, but also by the leather chemist who is pressed with everyday problems, since these problems usually require quick and easy methods of analysis and methods of application.

I feel the speaker is to be commended for working out a satisfactory and simple analysis for assaying most of the amino acids contained in collagen. The results are readily reproducible provided that, as he pointed out, the necessary precautions are taken.

The method provides separation of essentially all of the amino acids of collagen as indicated and it should be useful in studying or evaluating the degradation of collagen

The steps taken to iron out the many difficulties and to provide a simple technique have been presented as a result of a very thorough study. I have had the opportunity of studying in detail the two papers from which this talk was put together, and all of that information has not been presented today.

It was necessary to simplify this technique. There were many attempts before the true pattern was obtained. This technique of analysis of a biochemical entitity like collagen, which accounts for 96.6 per cent of the amino content, by isolating most of the amino acids, is very good. Adding a value for amide nitrogen to the amino acid isolated by the technique gives a material balance of 99.9 per cent.

If we can do as well with our standard ALCA analyses for leather, we feel we have accomplished a very good material balance.

DR. KANAGY: I think this paper of Mr. Cassel's provides an excellent tool for further research in the structure of collagen.

You know that for the last few years considerable progress has been made in the studies of collagen by means of the electron microscope, and various physiochemical methods and thermodynamics. For a long time we have needed a method of determining the fundamental building blocks in collagen—the amino acids. It now may be possible to start from these building blocks and determine the sequence of occurrence of the amino acids in the collagen chains and possibly from here build up to the point to which the electron microscope people have worked down.

The method certainly could be used as a control for following the effects of liming and other treatments of that type in the tanneries and also, of course, for treatments such as Mr. Cassel has pointed out—the treatment with nitrous acid. Also, the method should be very valuable for studying the mechanisms of degradation in collagen. For instance, for a good many years we have had only the side chains on collagen to study, such as the arginine and aspartic and glutamic acids. Now we have a procedure for studying the other amino acids and finding out what happens to them.

It also should be an excellent procedure for studying the effects of various atomic radiations. We are now entering the atomic age and will have to find out sometime what happens to materials such as hide, leather, and so on, when atomic radiations act upon them. I think by a procedure of this type you should be able to do that.

This method has already been used as a confirmatory test for collagen. Since collagen is perhaps the only protein which contains hydroxyproline, the appearance of the hydroxyproline spot gives a fairly good confirmatory test for collagen. The development of this test provides a procedure long needed for future chemical tests on collagen.

DR. MCDERMOTT: What was the concentration of the collagen present in the hydrolysate?

MR. CASSEL: About 250 mg. of protein in 15 ml. of acid solution.

DR. MCDERMOTT: About a quarter of a gram. And you use that solution straight in your spotting on the filter paper?

MR. CASSEL: Yes. That is one of the interesting things about it. With these solvents, which apparently are strongly buffering, you do not need to drive off the hydrochloric acid before placing the hydrolysate on the paper. In other words, you do not have to go through the procedure of vacuum distilling hydrochloric acid from the hydrolysate.

DR. MCDERMOTT: Straight filtration and application of the material right out of the sealed tube?

MR. CASSEL: That is right.

Calfskins are valued in proportion to their strength and size. The French tanners, who are renowned for the excellence of their calf leather, use the skins taken from animals of five or six months of age. Those from calves of less than two months' age are very inferior, and only suitable for the manufacture of parchment.

—*Arts of Tanning and Currying*, Morfit, (1852).

Experimental leathers that resist action of powerful oxidants and reductants used as guided missile fuel have been developed by the Air Force. Method is said to have applications in manufacture of shoes for wear in industrial plants. Method involves chrome-tanning leather, treating it by new emulsion method, and depositing a polymeric film about five mils thick.

—*Industrial Research Newsletter*, Armour Research Foundation, March, 1956.

But, of course, the danger of overselling the results of research and development to some stockholders cannot be overlooked. Some of them may have to be cautioned in a manner similar to that reportedly used by a United States Army general to a dinner companion. When urged to simply put more engineers and scientists to work in order to solve his research and development problems, the general replied that the generation of the solution was somewhat akin to the gestation period in humans; it still took nine months more or less regardless of how many men were employed.

—*Research and Engineering*, January, 1956.

Modification of Some Reactive Groups of Collagen and the Effect on the Fixation of Tervalent Chromium Salts

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ABSTRACT

Inactivation of collagen side-chains by processes of acetylation and methylation indicate that both may reduce the ability of collagen to combine with either anionic or cationic tervalent chromium ions. At least two types of reaction may take place, both of which result in a combination which is not reversed by exhaustive washing. One of these reactions is the actual penetration of carboxyl radicals into the chromium ion with the formation of a co-ordination complex. The second involves attachment at other reactive centers of the collagen molecule, probably by means of hydrogen bonds. Only co-ordinate bonds have the necessary directional character to bring about the enhancement of hydrothermal stability which follows interchain cross-linking, a characteristic of chrome tanning. The number and nature of the ligands occupying co-ordination sites in the chromium complex prior to its reaction with collagen will influence the amounts of chromium bound by either of the postulated mechanisms.

INTRODUCTION

During recent years the study of the part played by the various active centers of the collagen molecule in the fixation of tervalent chromium salts has received increased attention. Bowes and Kenten (1, 2) developing the pioneer work of Thomas and Kelly (18) studied the effects of modifying the amino, carboxyl and guanidyl groups of collagen with various reagents, and then determined the irreversible fixation of chromium from solutions of basic chromium sulfate by these products. Work by Green (5) showed that the non-ionic hydroxyl groups also affected the fixation of chromium, a result which was in disagreement with the findings of Bowes and Kenten (2). Results published by Sykes (16) appeared to confirm the conclusion drawn by Bowes and Kenten, that the carboxyl groups were of primary importance, since the carboxymethylation of the collagen amino groups with sodium bromoacetate gave a substrate which, after tanning, showed both increased fixation of chromium and also greater hydrothermal stability. The latter is measured by the temperature at which moist collagen shrinks when heated and is an indication of the degree of cross-linking (8). It is unfortunate that Green did not report any hydrothermal stability data for the chrome tannage of his acetyl-collagens, as subsequent work by Sykes (17) corroborated the reduction of chromium fixation reported by Green but showed that there was no corresponding reduction in the enhancement of hydrothermal stability induced by the chrome tannage.

These results indicated that more than one type of reaction is taking place when normal collagen is allowed to react with chromium salts, a suggestion which had previously been put forward by Shuttleworth (13, 14, 15). In addition to fixation of chromium at the various active centers of the side-chains in collagen there is also the possibility of reaction with the peptide linkages (9, 15), although it is not to be expected that this reaction would confer any great stability on the collagen. The present investigation was conducted with a view to distinguishing between the types of reactions which may take place between the active centers present in collagen, particularly the amino, carboxyl and hydroxyl groups and tervalent chromium salts. In order that a more generalized picture might be obtained, not only was a cationic 33% basic chromium sulfate used but also an anionic oxalatochromiate.

METHODS

The source of collagen used in this work was calfskin which had been depilated by a lime-sodium sulfide treatment, neutralized with acid and washed free of salts. It was then dehydrated with acetone and extracted with petrolic ether in a cold soxhlet apparatus to remove grease. The purified skin was cut into small pieces measuring 5 x 5 mm. and into strips 7.5 x 1 cm. and stored until required.

Acetylation of collagen

The method described by Green, Ang and Lam (6) was used as a basis for this work. Collagen dried in a vacuum oven was treated with ten times its own weight of a mixture containing equal parts of acetic and acetic anhydride. Samples of collagen, both pieces and strips, were removed at various intervals up to 192 hours from the commencement of the reaction. This technique led to the preparation of seven samples of partially acetylated collagen containing from 0.28–1.51 millimoles acetyl/g. The excess of acetylating reagent was removed in all cases by extraction with acetone in a soxhlet apparatus.

A further series of acetylated products was prepared by treating an esterified collagen, containing 0.86 millimoles methoxyl/g., with the same acetylating mixture. Analysis showed that 0.38–1.62 millimoles/g. acetyl had been introduced.

Methylation of collagen

The method devised by Fraenkel-Conrat and Olcott (4) for esterifying soluble proteins was used with minor alterations. Collagen was treated with twenty times its own weight of methanol adjusted to 0.1 *N* with concentrated hydrochloric acid. Samples of collagen, both pieces and strips, were removed at various intervals up to 288 hours from the commencement of the reaction,

and washed free of acid with distilled water prior to acetone dehydration for storage. Up to 0.86 millimoles/g. methoxyl was introduced into the collagen by this treatment.

A second series of methylated products was prepared by treating acetylated collagen, containing 1.51 millimoles acetyl/g., with acidified methanol as described. Analysis showed that 0.28–0.81 millimoles/g. methoxyl had been introduced.

Cationic chromium solution

Chromium trioxide was dissolved in water and reduced by passing a stream of sulfur dioxide through the solution until no hexavalent chromium could be detected. After boiling for 30 minutes to remove the excess sulfur dioxide the solution was cooled. Next day sufficient sodium hydroxide was added to the solution to combine with one-third of the sulfate radicals, thus producing a salt of empirical formula $Cr(OH)SO_4$. This basic solution was diluted to contain 25.3g. Cr_2O_3/1., i.e., 0.167*M* and refluxed for 30 minutes.

Anionic chromium solution

A solution of potassium dioxalato-diaquo-chromiate was prepared by reducing hot potassium dichromate solution with the theoretical quantity of oxalic acid. Previous work by Gustavson (7) had shown that a pH of 5 was the optimum for the fixation of chromium by collagen from this complex. Accordingly, potassium hydroxide was added to the solution over a period of three days, until the correct pH had been attained. The amount used was approximately 90% of that required to form potassium dioxalatohydroxo-aquochromiate. The solution was diluted to 25.3 g. Cr_2O_3/1.

Chrome tanning

Samples were taken from the various modified collagens to include sufficient small squares for subsequent analysis and two strips for shrinkage temperature determinations. The protein was hydrated by soaking in distilled water for 24 hours and then added to the chromium solution, maintaining a ratio of 50 ml. chromium solution per gram dry collagen. The reaction was allowed to proceed with continuous agitation for three days in the case of the cationic solution and seven days in the case of the anionic solution; previous work showed that these periods were sufficient for the attainment of equilibrium. The final pH of the chromium sulfate solutions varied between pH 3.0–3.1, while the oxalatochromiate solutions showed an end pH of 4.8–4.9. The chromed collagen was washed in running distilled water for two days to remove uncombined chromium salts and air-dried prior to analysis.

Analytical methods

The various collagens were analyzed for total acetyl by hydrolysis in 2*N* sulfuric acid followed by steam distillation of liberated acetic acid (6), and for

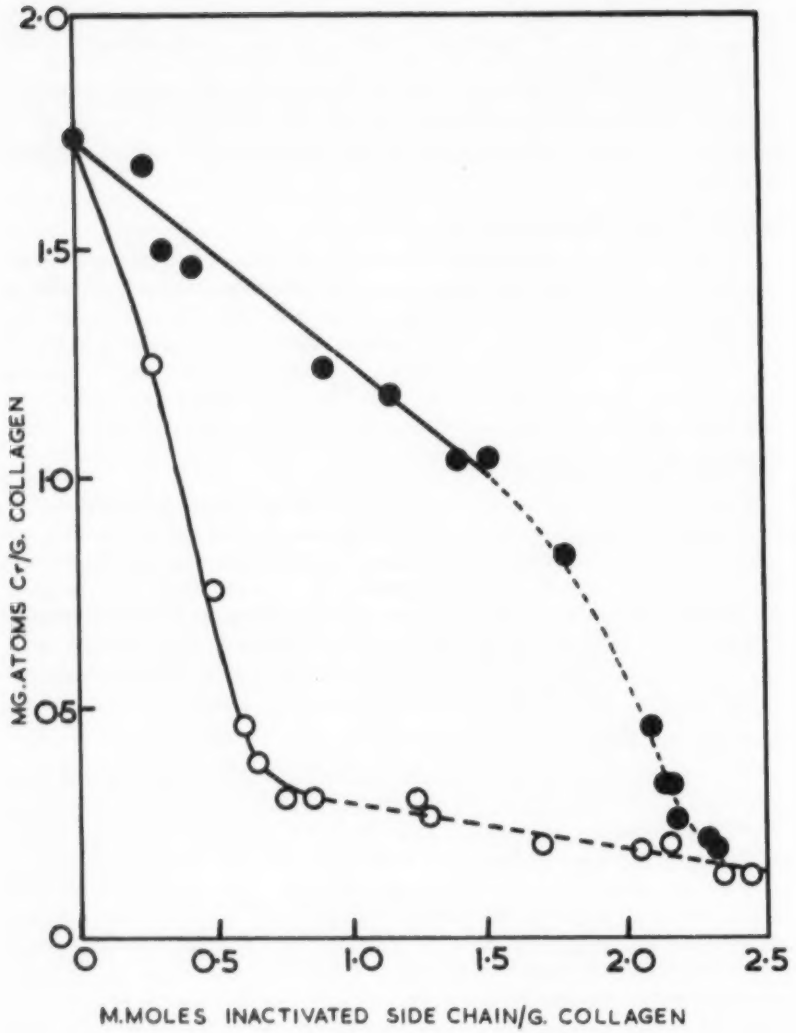

FIGURE 1.—Effect of progressive inactivation of the side-chains of collagen on the fixation of chromium from 33% basic chromic sulfate: ●, introduction of up to 1.51 millimoles acetyl/g. collagen, followed by introduction of up to 0.81 millimoles methoxyl/g. collagen; O, introduction of up to 0.86 millimoles methoxyl/g. collagen, followed by introduction of up to 1.62 millimoles acetyl/g. collagen. Full line indicates first substituent, broken line indicates second substituent.

methoxyl by the conventional semi-micro Zeisel technique using the bromine acetate absorbant of Vieböch and Brecher (19). The leathers were analyzed for chromium by the wet oxidation method using perchloric acid (3) and for nitrogen by the Kjeldahl method. Shrinkage temperatures of the collagens before and after tannage were determined by heating a sample, previously soaked for 24 hours in water, in liquid paraffin (2).

RESULTS

The effect which the degree of inactivation of the collagen side-chains has on the ability of the protein to combine with chromium is illustrated in

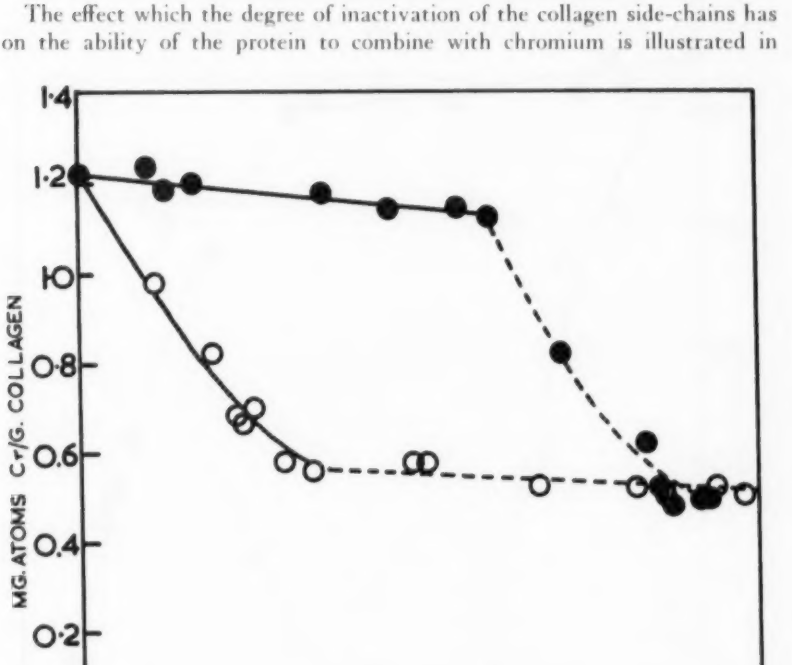

FIGURE 2.—Effect of progressive inactivation of the side-chains of collagen on the fixation of chromium from potassium oxalatochromiate: ●, introduction of up to 1.51 millimoles acetyl/g. collagen, followed by introduction of up to 0.81 millimoles methoxyl/g. collagen; O, introduction of up to 0.86 millimoles methoxyl/g. collagen, followed by introduction of up to 1.62 millimoles acetyl/g. collagen. Full line indicates first substituent, broken line indicates second substituent.

Figures 1 and 2, where the uptake of chromium has been plotted against the total number of side-chains inactivated. For both cationic and anionic chromium complexes the general trend is the same and it will be observed that the inactivation of amino and hydroxyl groups by acetylation has a much smaller effect on the fixation of chromium than the inactivation of the carboxyl ion by methylation. The combined effect of acetylation and esterification is the same regardless of the order in which the two treatments were given.

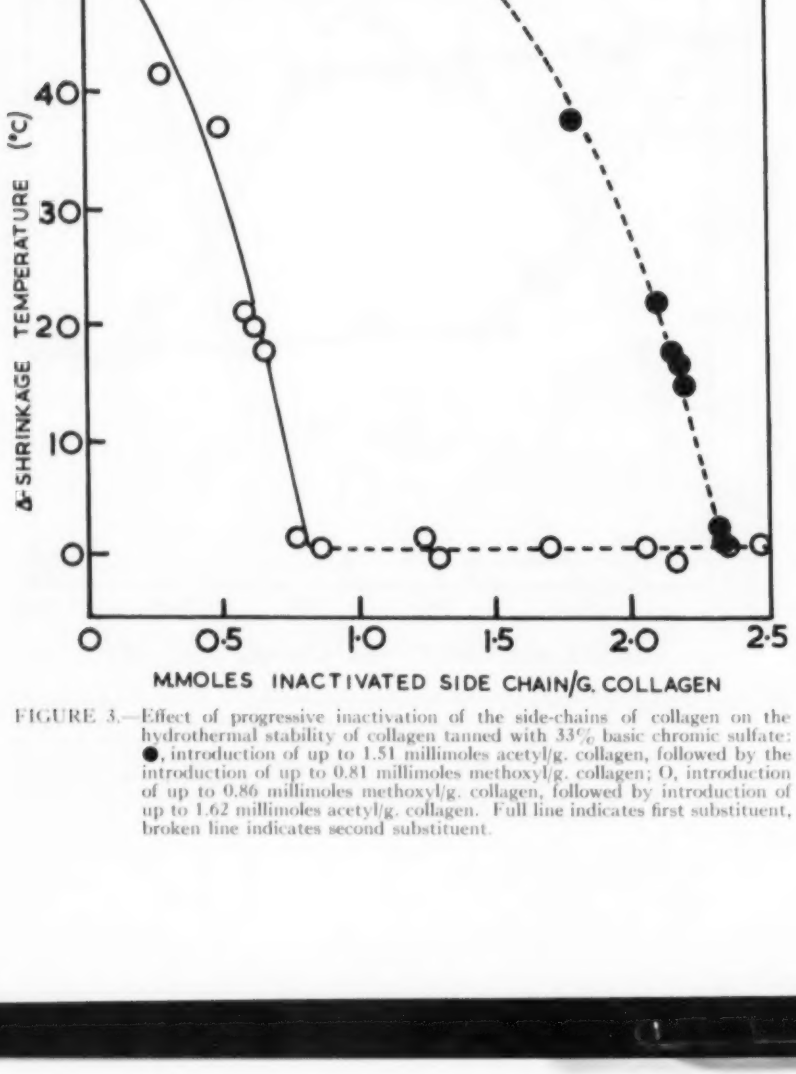

FIGURE 3.—Effect of progressive inactivation of the side-chains of collagen on the hydrothermal stability of collagen tanned with 33% basic chromic sulfate: ●, introduction of up to 1.51 millimoles acetyl/g. collagen, followed by the introduction of up to 0.81 millimoles methoxyl/g. collagen; O, introduction of up to 0.86 millimoles methoxyl/g. collagen, followed by introduction of up to 1.62 millimoles acetyl/g. collagen. Full line indicates first substituent, broken line indicates second substituent.

Similar trends are also observed in Figures 3 and 4 where data relating to the shrinkage temperature of the chrome-tanned collagens are recorded. These results have been recorded as $\triangle$-shrinkage temperature, which is the difference between the shrinkage temperature of the chromed collagen and the corresponding untanned collagen. This method of recording the results takes into account the decrease in the shrinkage temperature of collagen which is brought about by the various chemical pretreatments. This is a more accurate indication of the degree of stabilization of the protein molecule which has been brought about by the tanning agent than reference to the observed shrinkage temperature. The elimination of chromium fixation at

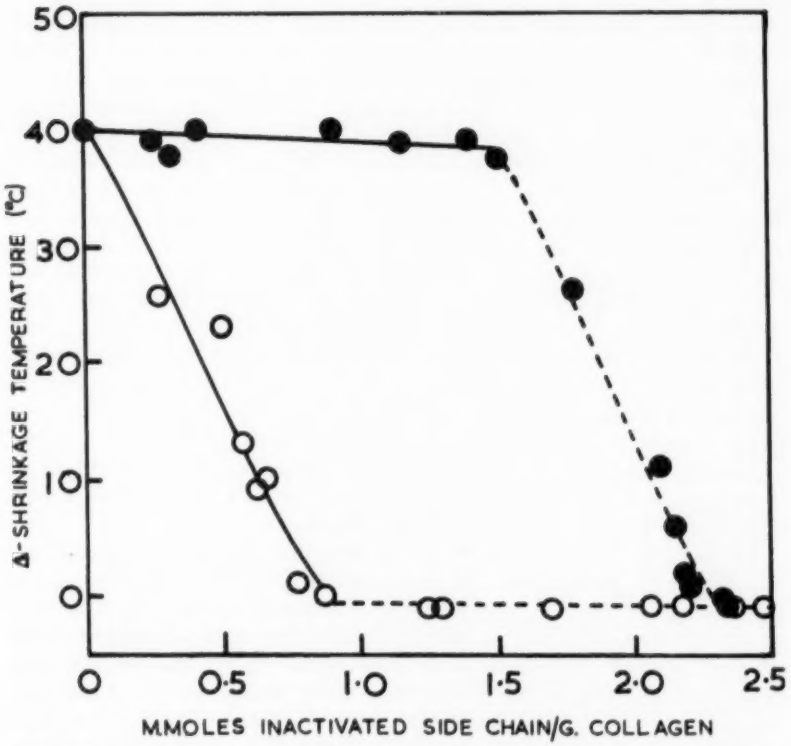

FIGURE 4.—Effect of progressive inactivation of the side-chains of collagen on the hydrothermal stability of collagen tanned with potassium oxalatochromiate: ●, introduction of up to 1.51 millimoles acetyl/g. collagen, followed by introduction of up to 0.81 millimoles methoxyl/g. collagen; O, introduction of up to 0.86 millimoles methoxyl/g. collagen, followed by introduction of up to 1.62 millimoles acetyl/g. collagen. Full line indicates first substituent, broken line indicates second substituent.

the carboxyl group has the effect of preventing any stabilization of the collagen molecule, although chromium is still bound at other centers. On the other hand Figures 3 and 4 show that the prevention of chromium fixation at either the amino or hydroxyl groups has a negligible effect on the hydrothermal stability of the chrome-tanned collagen.

DISCUSSION

Any investigation into the mechanism of the reaction between collagen and chromium salts is made extremely difficult by two factors. The first is the chemical constitution of the protein which provides a large number of sites where reaction with chromium might occur. The second is the complexity of the chromium ion which in addition to forming complexes by the replacement of co-ordinated water, can also form polynuclear ions either by the formation of olated –OH– bridges or by entry of polycarboxylic acids, where the carboxyl ions enter different co-ordination spheres. It was for this reason that two types of chromium complex were used in this investigation, the aim of which was to elucidate the general principles of the reaction rather than stoichiometric relationships. Steric hindrance in the fibrous protein is likely to prevent all the reactive side-chains in the collagen molecule from being equally available for reaction with a chromium ion whose molecular weight may be in the order of over 600. Indeed, the failure of the relatively small molecules used in acetylating and methylating collagen to react with all the available side-chains is an indication that the fine structure of the protein must play an even greater part in the penetration of the larger molecules used in tanning. Furthermore, until the sequence of amino acid residues in collagen has been elucidated and the intermolecular organization studied in more detail, any simple numerical relationships between the active side-chain content and the amount of irreversibly combined chromium should be regarded as purely fortuitous.

The reaction between many chromium salts and collagen is unique because not only is the protein protected from enzyme or bacterial degradation, but the stability of the fiber to moist heat is increased at the same time. In normal collagen the fibrous state is maintained by means of hydrogen bonds between adjacent polypeptide chains. Weir and Carter (20) consider that when heat is applied to this system the kinetic energy of thermal agitation coupled with thermal bombardment by water molecules will cause some break-down of the cross-linkages even at low temperatures. The number of cross-linkages broken at any particular instant will increase with temperature until, at some instant when a sufficiently large number of bonds are open, the molecule will collapse to a more stable configuration by chain folding. The effect of this reaction taking place in a number of centers at the molecular level will have the gross effect of causing a piece of skin to undergo

visible shrinkage. It is therefore to be expected that if chromium salts react with collagen to bring about a considerable increase in the shrinkage temperature of the protein, then intermolecular cross-links of greater stability than those naturally present must have been introduced. The actual degree of stabilization will depend on various factors such as the composition of the chromium complex ion and the type of bond which is formed. The possibility that chromium complexes may combine irreversibly with collagen without forming intermolecular bridges must not be overlooked.

Considering first the reaction of chromium salts with the carboxyl group, it is apparent that this mechanism must be the one of primary importance in distinguishing chrome tanning from salt formation which may occur with other metallic ions. The fixation of anionic chromium at the acidic centers rules out any question of simple salt formation. The fact that only the prevention of reaction with the carboxyl groups has any effect on the hydrothermal stability of the tanned collagen shows that cross-linking must only occur between the electro-negative carboxyl side-chains. From a study of the types of bond which can occur between organic ions and metallic complex-forming ions (11, 15), it would appear that only a co-ordination compound would possess the necessary directional character to produce a stabilizing effect similar to that produced in wool keratin by the covalent cystine bridge. It is, however, unlikely that all the carboxyl side-chains are equally available for cross-linking and some unifunctional co-ordination of chromium may be expected to take place, particularly when equilibrium is being reached (10). For complex formation to occur between a chromium ion and collagen, the electro-negative carboxyl ion present in the latter must be able to displace one of the ligands already in the complex; this may be either an aquo, hydroxy, or acid radical. As the stability of these various ligands is unequal, we have an explanation for the observation that both the amount of chromium fixed (Figures 1 and 2) and the resulting hydrothermal stability (Figures 3 and 4) vary with the nature of the chromium complex used for tanning.

Having shown that the distinguishing feature of chrome tanning is the introduction of cross-links with a directional character between the carboxyl radicals of adjacent collagen molecules, it is necessary to explain the fixation of chromium at other active centers. The reduction of the amount of chromium fixed by deaminized collagen at one time led to the assumption that the amino groups must play an important role in chrome tanning. However, the researches of Bowes and Kenten (1, 2), Weir and Carter (20) and Sykes (16) have all shown that although the total fixation of chromium may be affected it does not reduce the hydrothermal stability of the tanned collagen. Further, Shuttleworth (13) has used spectrophotometric data to demonstrate that under the aqueous acidic conditions encountered in chrome tanning, amine groups do not displace ligands already attached to the chromium nycleus. Similar considerations may be expected to apply in the case of

the basic guanidyl radical. In other work on the co-ordination of hydroxy groups to chromium, Shuttleworth (12) demonstrated that at pH values below 7.0 co-ordination could only occur if chelate ring formation was also possible. As this cannot occur with the hydroxy side-chains present in collagen, the conclusion must be drawn that co-ordination does not take place. To reconcile this evidence with the known fact that inactivation of the hydroxyl groups does reduce chromium fixation (5, 17, and Figures 1 and 2) it is necessary to postulate that the chromium is being held by other forces than co-ordination; hydrogen bonding would appear to be the most probable.

It is also possible for chromium to be bound at the keto-imide groups of the peptide link. Gustavson (9) has demonstrated that 8*M* urea solution, a reactant which he considers to be specifically directed to the peptide groups, may displace chromium which is stable to exhaustive washing. As this partial removal of chromium has a negligible effect on the hydrothermal stability of the tanned collagen, any chromium bound by this reaction cannot be considered to have formed the co-ordination compounds capable of cross-linking. It would appear probable that the chromium bound by the collagen after its inactivation by acetylation and esterification (points on the extreme right of Figures 1 and 2) is attached by hydrogen bonds at the peptide link.

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A Combined Solvent Extraction and Tanning Process

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ABSTRACT

Dehaired hides were tanned, without preliminary dehydration, with a suspension of solid tanning material in acetone. The wet hides provided enough water to effect solution of the tannin. This system eliminates two steps of other solvent tanning systems: the dehydration of the pelt and the preparation of a tannin solution in the solvent. The results of small-scale tanning tests are promising.

INTRODUCTION

The use of organic solvents as an aid in the extraction of tannin and in the tanning of heavy leather has been suggested. Luvisi, Cordon, Beebe and Rogers (4) in 1949 proposed the extraction of tannin from canaigre by aqueous solutions of various alcohols, or preferably of acetone. Roddy (6) in 1943 published the results of tanning tests using acetone solutions of tanning material. Kremen in 1955 (3) demonstrated the possible advantages of such tannages.

As shown by Stather, Lauffmann and Bau Miau (7) in 1936, pure acetone is a poor solvent for tannin. Of all the common tanning materials, only quebracho is sufficiently soluble to be of use in a system such as proposed by Kremen. Wattle is moderately soluble. However, mixtures of acetone and water, in a wide range of concentrations, are very good solvents for tannins. The use of such mixtures greatly increases the speed of extraction and the amount of tannin extracted compared with either pure acetone or water.

The cost of an organic solvent either for tannin extraction or for tanning would be prohibitive unless the solvent were recovered. Even in this case, the cost of the recovery process would be considerable. If tannin were extracted by an organic solvent-and-water process, and the extract thus prepared were used for tanning by a solvent process, two recovery steps would be required. However, if the two processes could be combined, the advantages of both could be obtained with only one recovery step. We have devised such a process using acetone as a solvent. This process has a further advantage over other solvent processes in that it is not necessary to dehydrate the hides before tannage. Although applicable to any tanning material, it is particularly advantageous for materials of high tannin content, such as canaigre roots or wattle bark, which were used in these tests.

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TANNING PROCEDURE

The hides, prepared as usual for tanning (by soaking, liming, unhairing, fleshing, and washing or bating slightly as desired), are put into a tanning drum. The calculated amount of finely ground tanning material is then added together with the required amount of acetone. The drum is turned intermittently at a slow rate for several hours. Penetration of tannin into the hide is slow at first because of the low solubility of tannin in acetone. However, as water diffuses from the hide, a solution of acetone and water is formed which is a better solvent for tannin. As the solution penetrates into the hide some combination takes place between the hide and the tannin because of the presence of water in the hide. Because the concentration of tannin in the solution is low at first and increases gradually, full penetration is obtained without any trace of case hardening. The time required for penetration is about 16 hours. This is somewhat longer than the time required for penetration in other solvent tannages but since dehydration of the hides is not required, the total time is approximately the same. In addition, the cost of the dehydration process is eliminated. The moderate amount of tannage taking place during the impregnation by the acetone solution is an advantage in that it puts the hide in better condition for subsequent processing.

After complete penetration of tannin from the acetone solution, the hides are drained and treated with a strong, aqueous tanning liquor prepared as described later. This corresponds to the usual "extracting" procedure in tanning. The speed of the drums should be considerably slower than the usual speed of "extract" drums to prevent damage to the hides before they are sufficiently tanned. The drums should be turned intermittently at first. The "extracting" step will thus require somewhat more time than the usual extracting procedure but still will not require more than three or four hours. After "extracting", the leather is finished by normal procedures. The time required from beamhouse to bleach vats should be three or four days.

The acetone is recovered from the solution by distillation. The remaining aqueous solution is filtered and, if desired, sulfited. This liquor is used for the extracting step. The process may be adjusted so that the amount of liquor prepared from the acetone solution is exactly that required for the "extracting" step, or so that addition of a slight amount of commercial extract will be required.

EXPERIMENTAL

Some of the factors involved in this process are: the kind of tanning material used, the size of the grind, the duration of each step, and the manner of "extracting". The following experiments are indicative of the partial evaluation of some of these factors. The results are summarized in Table I.

In Experiments 1 to 6, both stages of the process were carried out in a Meissner mill, 24 inches in diameter, making eight turns a minute. This was run intermittently for five minutes of every half-hour. All hide pieces were cut from the bend portion of a hide which had been prepared in the usual manner for tanning.

TABLE I

SUMMARY OF EXPERIMENTS

Experiment No.	Hide Wgt.	Tanning Material Source*	Tanning Material	Grind Mesh	Volume of Acetone	Amt. 40° Tw. Liquor for Extracting	Time in Acetone	Leather Yield†	Tannin in Spents
	g.		g.		l.	ml.	hr.	%	%
1	227	Canaigre	300	20	1.3	140	24	71.8	7.4
	223							70.9	
2	249	Canaigre	166	9	0.44	74	8	56.0	12.3
3	217	Canaigre	145	20	0.39	66	8	67.0	5.9
4	282	Canaigre	189	20	0.75	85	24	76.9	5.8
5	318	Wattle	230	20	1.85	125	24	69.6	2.7
6	337	Wattle	300	20	1.86	165	24	70.7	3.2
7	4332	Canaigre	6,000	20	75.6	50,000	24	71.9‡	9.9
	4453							70.9	
8	4830	Wattle	4,540	20	75.6	50,000	24	72.8	13.5
	4850							73.0	

*Tannin in material as used—canaigre 33%; wattle 39%.
†Finished weight as percentage of white weight.
‡Yields of comparable bends tanned at a commercial tannery were 77.5 and 77.3%.

The spents were analyzed by the official methods of the American Leather Chemists Association (1) except that the method of Luvisi and Rogers (5) was used to prepare the analytical solution of the canaigre.

Experiment 1.—Two pieces were tanned as indicated in Table I. After impregnation with tannin in the acetone solution they were taken out and wrapped in cloth to prevent drying out. The total liquor, including the rinsings, was distilled to recover the acetone. The aqueous solution was settled by standing for four hours and the supernatant evaporated under vacuum to give a 40° Tw. liquor. This was treated with 5% sodium bisulfite based on the weight of solids. This liquor was swabbed and rubbed into the leather pieces to simulate the effect of "extracting". The pieces were sammied for two days, after which they were bleached, oiled and dried. The total operating time from beamhouse to oiling was three days. The leather was firm, of good color, well and uniformly filled with tannin and had no drawn grain or other visible defect. Considering the peculiar nature of canaigre, the analysis of the spents indicated that a satisfactory extraction of the tannin had been obtained.

Experiments 2 and 3.—These indicate the effect of fineness of grind of the tanning material and of time in the acetone solution on the pick-up of tannin. In Experiment 2 penetration of tannin into the hide was unsatisfactory, and leather yields were low. In Experiment 3 the use of finely ground material resulted in satisfactory tanning even in eight hours. A somewhat longer period might be advantageous, since exposure to the acetone solution for 24 hours resulted in a definitely higher yield.

Experiment 4.—In the preceding tests it was necessary to hold the leather pieces one day after taking them from the acetone solution, until the acetone had been distilled and the liquors concentrated. This would not be done in practice. Therefore, a test was made in which the leather, after being removed from the acetone, was treated immediately with an extract equivalent in quantity and composition to that which could have been produced from the acetone liquor. Leather of comparable quality and good yields was obtained.

Experiments 5 and 6.—These experiments were conducted in the same manner as in Experiment 1, except that wattle bark was used as the source of tannin. The leather produced was of good quality. The spents were analyzed by the official methods of the American Leather Chemists Association (1).

In all the preceding experiments the leather yields give an approximation of what might be expected in practice but since the pieces were cut from different portions of the same hide, variations in yield might be expected.

In Experiments 7 and 8 tannage was carried out on a larger scale, using bends. Because of restrictions upon the use of volatile solvents, the tannage could not be carried out in the most desirable manner, which would be in drums or in enclosed vats with vigorous stirring. For the tannage a vat 4½ inches wide, and long and deep enough for a bend was used. To keep the tanning material in suspension, a stirrer was placed at each end of the vat. Each stirrer had a vane near the bottom of the vat, and one about halfway to the top. These vanes were only two inches in diameter, however, and did not keep the powdered material in the state of suspension necessary for the most efficient extraction. No equipment was available for recovery of the solvent and preparation of the "extracting" liquor. Therefore, for this purpose a liquor was made from powdered extracts; for the canaigre tannage a sulfited canaigre extract was used and for the wattle tannage a sulfited quebracho extract. Since the size of the tanning drum was disproportionate to the size of the bends, it was necessary to use a larger "float" than usual. For these reasons, a satisfactory tannin balance cannot be calculated for these experiments. This does not affect the evaluation of the leather produced.

Experiment 7.—Two hides were obtained from a tannery cold pool. Two bends were cut from each hide, one of which was sent to the tannery to be

tanned and finished in the usual manner. The other was tanned by the solvent process at the laboratory. After immersing the bends in the acetone, the stirrers were run for six hours, the settled material on the bottom being occasionally mixed with a paddle. The bends remained in the liquor overnight without stirring. The following morning the stirrers were run for two hours. The leather was removed, drained for ½ hour, and placed in a tanning drum containing sulfited canaigre extract of 40° Tw. The drum was turned intermittently for six hours—five minutes turning and 25 minutes standing. The bends were left in the drum overnight without turning. The drum was then turned slowly and steadily for two hours. The bends were taken out, sammied for two days, and returned to the tannery for bleaching, oiling, and finishing. They were saved for comparison with the bends finished by the regular process. The total time between white pool and bleach was seven days; the actual operating time was five days. The leather produced was uniformly tanned throughout the whole cross section; there was no drawn grain or other defect, and the color was exceptionally good. A slightly "empty" feel to the leather was confirmed by the yields, which were somewhat low for the laboratory as compared to the tannery bends. The rather low yields of the leather and high tannin content of the spents were probably due to the somewhat unsatisfactory method of operation. The analysis of the leather obtained is shown in Table II.

TABLE II

ANALYSES OF FINISHED BENDS

CALCULATED ON MOISTURE-FREE BASIS

	Experiment 7		Experiment 8
	Solvent-Tanned with Canaigre	*Commercially Tanned**	*Solvent-Tanned with Wattle*
Petroleum ether extract (%)	5.4	6.0	4.8
Insoluble ash (%)	0.2	0.2	0.3
Hide substance (%)	43.4	34.4	40.4
Soluble matter (%)	29.3	37.9	31.5
Combined tannin (%)	21.7	21.5	23.0
Total (%)	100.0	100.0	100.0
Degree of tannage (%)	50.1	62.7	56.9
Soluble nontannin (%)	19.8	27.8	19.0
Soluble tannin (%)	9.5	10.1	10.3
pH †	4.3	3.8	4.4

*Comparable bends tanned with usual tanning blend at a commercial tannery.

†Determined on air-dry leather according to official methods of the American Leather Chemists Association.(2).

Experiment 8.—This tannage was conducted in a manner similar to Experiment 7, except that wattle was used in place of canaigre. An excess was

used in order to produce a well filled piece of leather, although it was felt that this would increase the tannin remaining in the spents. No tannery comparisons were made of this tannage. Both bends of the hide were used for the solvent tannage. The tanning operation was the same as in Experiment 7, except that sulfited quebracho was used for the second stage. The yields were somewhat better than in Experiment 7, but, as expected, the tannin remaining in the spents was high. The leather was of good quality and did not have the "empty" feel of the canaigre bends. Analysis of the leather is shown in Table II. The experiment might have been more realistic had it been possible to use an extract for the second stage prepared from the acetone liquor of the first stage. However, tests have indicated that the use of an equivalent solution does not influence the results to an appreciable extent.

DISCUSSION

The advantages of solvent tannage, as outlined by Kremen, would also apply to this tannage: the rocker and layaway yards are eliminated and the time required for the tanning process is reduced. The inventory and labor needed are consequently reduced, although the advantage is at least counterbalanced by the necessity for a solvent-recovery process. The shorter time of tannage also allows a more rapid response to changing conditions such as fluctuations in hide prices or demands for different types of leather. Other advantages are reduction of sewage-disposal problems and possible use of the solvent to introduce desirable materials into the leather. The disadvantages in the use of a volatile solvent are, in addition to the requirements of a recovery system, the loss of solvent, the necessity of adopting safety measures against fire, and the fact that existing tannery equipment cannot be used without modification.

The advantages of the method described here are that it combines tanning and extraction into one operation, and uses a more efficient means of extracting the tannin from the raw material. Furthermore, it does not require dehydration of the hides before tanning.

The method would also be applicable to other tanning materials, but for operational and economic reasons it is probably most suited to those of high tannin content, such as canaigre roots or wattle bark. It is possible that the advantages of using hides which have not been dehydrated might be extended to the use of tanning extracts instead of raw tanning materials as suggested by Roddy (6). In this case the extract would be added to acetone at intervals in gradually increasing portions.

The leather yields and the analyses indicate that the leathers were not as thoroughly tanned as normal leather. However, the conditions used were not optimum. It seems quite possible that by improving the conditions of tanning and modifying the finishing processes, yields of leather comparable to those of usual tanning operations may be obtained.

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AVERAGE NUMBER OF MEN EMPLOYED IN THE PRATTSVILLE TANNERY WITH THEIR WAGES PER MONTH

BEAMHOUSE

	No. of hands	Pay per Month	
Foreman	1	$32	$32
Choresmen	2	12 (and board $6)	36
Beamsmen	12	14 (and board $6)	240

IN THE YARD

Foreman	1	50	50
Handling and laying away	8	12 (and board $6)	144
Brushing leather	6	12 (and board $6)	108
Nightman to leeches	1	14 (and board $6)	20
Grinding bark by day	1	12 (and board $6)	18
Grinding bark by night	1	14 (and board $6)	20
Wheeling bark	4	12 (and board $6)	72
Filling and pitching leeches	3	24 and board $6)	90

—*Arts of Tanning and Currying*, Morfit, (1852).

A literature survey on tannery byproducts pointed to the need for research in the following areas: nutritional investigations of fleshings, hide, and leather scrap; study of the development of fibers and filaments by means of nonaqueous solvents; development of moldable materials from hide and leather residues, and modification of animal hair for felting.

—*Annual Report*, Armour Research Foundation, (1955).

LIFE LINES

Brief Biographies of Our Contributors

CLARENCE W. BEEBE is Supervisor, Tanning Materials Unit, Eastern Utilization Research Branch, U. S. Department of Agriculture. He has been associated with this laboratory, or its predecessor, for 27 years. Before entering the government service he worked as a chemist for Kullman, Salz and Co., tanners, from 1917 to 1928. He graduated from the University of California in 1917.

JAMES M. CASSEL received his B. S. at Washington and Jefferson College and his M. S. degree at Georgetown University. He has been employed in the Leather Section of the National Bureau of Standards for ten years, and is at present serving as the Assistant Section Chief. He is also advisor for the trainees assigned to the Organic and Fibrous Materials Division during each summer. He has been a member of the American Leather Chemists Association and the American Chemical Society since 1948.

MARY V. HANNIGAN, a graduate of Chestnut Hill College, has been with the Eastern Utilization Research Branch since 1953, before which she was employed successively by Frankford Arsenal and the Quartermaster Corps Research and Development Center. Her present field of research is mineral and resin tannages.

DR. ROBERT M. LOLLAR, a very frequent contributor to this Journal, is Associate Professor in the Department of Tanning Research, University of Cincinnati. He received his M. S. and Ph. D. degrees from the same university. After four years with Best Foods, Inc., he joined the staff of the Tanners' Council Research Laboratory in 1941. He was the recipient of the Alsop Award in 1954.

JEROME S. ROGERS is one of our dozen oldest members; he joined the Association in 1912. He retired as head of the Hides, Tanning Materials, and Leather Section, Eastern Utilization Research Branch, U.S.D.A., in 1954, after 26 years of service. From 1918 to 1937 he was in charge of the laboratory of Kistler, Lesh & Co., later absorbed by International Shoe Co. He holds a B. S. from Syracuse and a master's degree from the University of Illinois. He was President of this Association, 1924-26, and served on many technical committees. As a fitting tribute to a lifetime of service, he received the Alsop Award in 1955.

DR. R. L. SYKES graduated with First Class Honors from Leeds University in 1950, and took his Ph. D. from the same institution in 1952. He was award-

ed the LeBlanc Medal by the Faculty of Technology of Leeds (1950), held the Procter Memorial Fellowship (1950–51), and received the Donald Burton Prize of the Society of Leather Trades Chemists in 1953. After 18 months in the British Colonial Service in East Africa, where he worked in an advisory capacity to the hides, skins and leather industries, he joined the Leather Industries Research Institute, Grahamstown, South Africa, as Senior Research Officer in 1954. His brief professional career has already resulted in 15 publications in various technical and scientific journals.

C. David Wilson, after graduating from Northwestern University, worked in the Pioneering Research Division of E. I. duPont de Nemours & Co., Inc., for one year before joining the Fred Rueping Leather Company in 1948. Later he spent two years at Lehigh University under the late Dr. Edwin R. Theis. Returning to Fond du Lac, he served as Director of Chemical Research and Development at Rueping until October, 1952. Since then he has been Assistant Tanner, and a member of the Rueping Board of Directors.

BOOT TOP LIQUID

Solution of muriate of tin	3 drachms
French chalk (in powder)	1 ounce
Salt of sorrel	½ ounce
Flake white	1 ounce
Burnt alum	½ ounce
Cuttlefish bones (powdered)	1 ounce
White arsenic	1 ounce
Boiling water	1 quart

—*Henley's 20th Century Home and Workshop Formulas, Receipts and Processes*, (1927).

LIQUID BLACKING

The following formula makes a product of excellent quality:

Ivory black	120 parts
Brown sugar	90 parts
Olive oil	15 parts
Stale beer	500 parts

Mix the black, sugar and olive oil into a smooth paste, adding the beer a little at a time, under constant stirring. Let stand 24 hours, then put into flasks, lightly stoppered.

—*Henley's 20th Century Home and Workshop Formulas, Receipts and Processes*, (1927).

ALCA NEWS

Proceedings, Reports, Notices and News
of the
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Curtis S. Peterson passed away at his home in Topsfield, Mass., on March 19, 1956, after a long illness. After graduation from Lewis Institute of Technology, Chicago, in 1925, he served as chemist, tanner, or consultant in many prominent firms in the leather industry. For the past four years he was Chief Chemist and Superintendent of Kirstein Leather Company, Peabody, Mass. He joined the Association as an Associate Member in 1952 and became an Active Member in 1956.

A.L.C.A.–A.S.T.M. JOINT COMMITTEE ON LEATHER

At the American Leather Chemists Convention in 1955, it was voted to make arrangements with the American Society for Testing Materials for a Joint Committee to establish standard methods of testing leather. It was felt by members that publication under the A.S.T.M. name would bring world-wide recognition to such methods. When the subject was first discussed with A.S.T.M. personnel, they mentioned that their Society had been approached on a number of occasions about standard methods for testing leather. Therefore the A.S.T.M. was more than willing to work with our organization in establishing such standards.

On March 13, an organization meeting was held at the A.S.T.M. Headquarters in Philadelphia. Invitations were sent to a number of companies and organizations representing producers and consumers of leather as well as people who have a general interest in it. The make-up of the Joint Committee according to A.S.T.M. procedures will be to have the number of producers of leather no greater than the number of consumers and general interest representatives combined.

Officers elected at the meeting were:

Chairman: Dr. Joseph R. Kanagy, National Bureau of Standards
Vice-Chairman: Mr. R. J. Wirshing, General Motors Corp.
Secretary: Mr. M. H. Battles, A. C. Lawrence Leather Co.

These officers will serve both in the Advisory Committee and in the General Committee. The Advisory Committee also includes: Mr. A. N. Kay, Howes Leather Co.; Mr. B. L. Lewis, Tinius Olsen Testing Machine Co.; Mr. Mieth Maeser, United Shoe Machinery Corp.,; Mr. G. H. Meyer, Liberty Dressing Co.; Dr. R. Shaw, Rohm & Haas Company; and Mr. J. N. Smith, E. F. Houghton & Co.

The scope of this committee's work was defined as "the development, evaluation of significance, and standardization of methods of sampling and testing, and the definition of terms pertaining to leather." Initially only physical test methods will receive attention; chemical methods will be considered later.

It was decided that the following sub-committees would be established and begin to function as soon as possible:

I. Nomenclature, definitions, and applicability
II. Sampling and conditions for physical testing
III. General physical testing
IV. Research
V. Editorial

The exact functions and areas of responsibility of each of these committees will be more clearly defined at a later date. Under sub-committee III it was decided that sub-divisions into working committees would be made on the basis of the type of test rather than the type of leather. A tentative list of working committees was established at an Advisory Committee meeting held later the same day. This will be published after approval by the Joint Committee.

A rough draft of the by-laws was read and discussed at some length. A revision will be sent to members for consideration prior to the next meeting when the subject will again be taken up.

When a method has been accepted by the Joint Committee, it will be published through the A.S.T.M. but will bear the seals of both organizations. This is not a new practice for A.S.T.M., as it has published many methods under joint sponsorship with several other organizations in the past.

A questionnaire is being sent to all those who are now members of the Joint Committee to determine the sub-committees and working committees on which they wish to serve.

Anyone wishing to participate in this Joint Committee should so advise the secretary of the Committee (Mr. Battles) in writing as soon as possible since the next meeting is expected to be in June. Participants must ordinarily be members of either the A.L.C.A. or A.S.T.M., but the Advisory Committee may waive this requirement.

Necrology—1955

The Association suffered the loss of nine members by death in 1955. Their names, the year in which they joined the Association, and their last professional connection are given below:

Lester H. Armstrong (Associate Member), 1951, Diamond Alkali Co.
M. Baran, 1928, Peter Baran & Sons
W. H. Barrett (Associate Member), 1933, Barrett & Co., Inc.
Edwin I. Chalmers (Associate Member), 1947, E. I. Chalmers & Co., Inc.
James E. Connelly (Life Member), 1912
Charles W. Lizer (Associate Member), 1952, W. B. Byron & Sons, Inc.
Arthur Sauer (Associate Member), 1935, Tanimex Corporation
J. Stodola (Life Member), 1914, retired
Dean Williams (Life Member), 1923, L. H. Lincoln & Son, Inc.

Notice to Authors

Authors are requested to introduce each paper submitted to the Journal by an abstract of the article. Articles should also be accompanied by a brief biography of the author(s) for inclusion in "Life Lines", a new feature in the Journal. Unnecessary correspondence will also be avoided if a notation is attached to the copy indicating where the author desires galley proofs to be sent.

"Shavings"

The editors contemplate introducing in the Journal a new feature to be entitled either "Shavings" or "Trimmings" and to include personal news of a professional nature about members of the Association. Considered appropriate for such a section is news concerning transfers, promotions, retirements, honors (civic or professional), writings, speeches, etc. Members are urgently invited to submit items of this kind about themselves or fellow members to the Managing Editor.

WORKING ON THE BEAM

After the skins have been prepared for the separation of the hair upon them . . . the next procedure is to remove it entirely by working them upon the beam . . . After the hair is completely removed, the skin is washed . . . and is then subjected to the following operations.

1. The flesh and other parts not properly belonging to the skin, are removed with a sharp knife . . . and the skin is again washed and soaked in fresh water.

2. The projecting filaments or shreds, and those parts of the borders of the skin that are thicker than the rest, are cut off, and the skin is again immersed in fresh water.

3. The hair side is then well rubbed and smoothed with a stone, similar to that used for sharpening the knife blades. This done, the skin is dipped for the third time in fresh water.

4. Both sides are well scraped and smoothed with a knife having a curved blade, so as to equalize the surfaces and remove all foreign particles.

A dozen skins can be worked by one man in the course of a day.

—*Arts of Tanning and Currying*, Morfit, (1852)

ABSTRACTS

Liming of Animal Skin. III. Sulfur Compounds Produced in Lime Liquor. Harukazu Toyoda. *Repts. Govt. Chem. Ind. Research Inst., Tokyo,* **48,** 277-87 (1953); *Chem. Abstr.,* **50,** 591*g* (1956).—Rabbit hair was immersed at 25°C. for 1 to 20 days in 0.2*N* NaOH or $Ca(OH)_2$ suspension, alone or with 1 per cent monomethylamine or 0.02 *M* Na_2S, and the hair and liquor were analyzed periodically for total N and total S and its compounds. The keratin dissolved from the hair by the alkaline treatment was found to decompose rapidly within 24 hours, and then to be oxidized successively in longer time to sulfide, polysulfide, sulfite, and thiosulfate. All these compounds except sulfite showed depilatory action when added to lime liquor. **IV. Depilatory Action of Dimethylamine.** *Ibid.,* **48,** 288-97.—Mono- and dimethylamine (but not trimethylamine) were depilatory. The depilatory action of dimethylamine was accelerated with higher concentration and temperature, independent of the ratio of liquor to skin. The acceleration was continued even when the skin was dipped for a short while in a lime liquor containing dimethylamine, and then transferred to a plain lime liquor, but not when the skin was pretreated with lime liquor alone and then transferred to the liquor containing dimethylamine. Addition of inorganic acids weakened the depilatory action, and that of Na_2S strengthened it. Aqueous $Ba(OH)_2$, at pH below 12, was hardly depilatory, but ammonia, and especially mono- and dimethylamine were depilatory even at lower pH values. With higher concentrations or longer immersion the depilation became difficult because of the constriction of the follicles by swelling. **V. Action of Dimethylamine on Hide and Hair.** *Ibid.,* **48,** 298-302.—Dimethylamine added to lime liquor did not markedly affect the hydrolysis of hide but caused its swelling, however slightly, and its softening by the separation of collagen fibers. The dimethylamine was absorbed rapidly by the hide to an equilibrium at about 15 per cent, but did not appreciably affect the saponification of the fat of the hide (in the usual concentrations), nor did Na_2S. The hydrolysis of hair was increased with higher concentrations of dimethylamine at higher temperatures in longer liming time, and its solubility in alkali was increased with higher concentrations of dimethylamine relatively independent of the liming temperature and time.

The Distinction Between Collagen and Keratin in Lime Liquors. D. Wegerle and H. Zahn. *Das Leder,* **6,** 298 (1955).—In leather manufacture the source of dissolved protein decomposition products in lime liquors is of considerable interest. Components of the epidermis are expected but the occurrence of collagen fragments points to an undesirable attack on the corium. Formerly, distinction between decomposition products of collagen and keratin was not possible, but now it can be made chromatographically if their amino acid composition differs. Data from the literature show that there is 14% hydroxyproline in collagen, none in wool (keratin); 11.3% cystine in wool, none in collagen; 6.4% tyrosine in wool, 0.9% in collagen. The ratio of glycine to serine is 10 to 1 for collagen and 0.55 to 1 for wool. The following materials were prepared and examined: A. 100 ml. of calfskin enzymatic lime liquor containing sodium hydroxide and sulfhydrate was evaporated at 90° and dried. It contained 862 mg. of dry matter and 296 mg. of protein per 100 ml. B. 500 ml. of the above liquor was dialyzed against water, and acidified to pH 3. The precipitate contained 66 mg. of protein. C. The filtrate from B was concentrated in a vacuum to give 232 mg. of dry matter. D. Precipitated material obtained by adding 20% trichloroacetic acid to filtered lime liquor A until the pH was lowered to 3-4. E. Precipitate formed by bringing a dialyzed lime liquor to pH 7. F - H. Grain-free split material was limed for 50 days at room temperature after which the liquor was filtered to give a cloudy, yellowish liquid containing 0.53 g. of protein per 100 ml. of solution. 500 ml. of this liquor was dialyzed against water for 3 days with 3 changes of water. The pH of the dialyzate

was 8. F. 250 ml. of this liquor was acidified to pH 5. A jelly-like precipitate formed that contained 60% of the total protein. G. 250 ml. of the liquor was acidified to pH 5, then all (precipitate and liquid) was dried. H. 100 ml. of lime liquor from the split material without dialysis was concentrated at 35° to 10 ml. J. Normal calfskin lime liquor containing sodium sulfhydrate was neutralized. After extraction of the precipitate with sodium hydroxide, the protein was precipitated isoelectrically, reprecipitated, then dried at 35°. For identification by means of 2-dimensional, 6-day, paper chromatograms, 100 mg. of material was hydrolyzed with 1 ml. of 6 *N* hydrochloric acid, the acid was removed and the residue dissolved in 1 ml. of water. The first solvent was secondary butyl alcohol, 75 parts; 90-percent formic acid, 15 parts; and water, 10 parts. The second solvent was 80-percent phenol. Preparations A, B, C, D and J consisted principally of keratin as the chromatograms showed spots for tyrosine and cystine, none for hydroxyproline and spots of approximately equal size for serine and glycine. Preparations F and G showed hydroxyproline spots, none for cystine or tyrosine and a larger spot for glycine than for serine, thus indicating these preparations contained chiefly collagen. Preparation E contained hydroxyproline and no tyrosine but also cystine and approximately equal amounts of glycine and serine; it was therefore collagen mixed with keratin. Preparation H was not hydrolyzed; the chromatogram had ninhydrin-positive spots that were partly free amino acids (glycine, alanine, etc.) and partly lower peptides. The results show that the usual short, sharp lime dissolves only components of the epidermis and hair. A long-time liming in white lime dissolves collagen. Bowes (*Biochem. Jour.*, **43,** 365; *Research*, **4,** 155) found that 5-10% of the collagen dissolved when oxhide was treated for 14 days at 20° in a lime liquor containing caustic soda to give a pH of 13.3. The dissolved collagen was present, partly as large molecules which precipitated on neutralization of the solution and partly as amino acids and lower peptides. These observations are confirmed by the present work. Bowes, Elliot and Moss (in *Nature and Structure of Collagen* by J. T. Randall, p. 199) reported that on treatment of collagen with alkali a material dissolved that contained very little hydroxyproline but a relatively large amount of tyrosine. They however did not consider the cystine content or the glycine to serine ratio. In the present work the grain-free split was essentially collagen. The isolated protein fraction (preparations F and G) gave a typical collagen chromatogram in which tyrosine was absent and hydroxyproline strong. I.D.C.

A Simple Method for Determining Tanning and Combining Values. G. Reich. *Das Leder*, **6,** 228 (1955).—The Stather-Herfeld method for determining tan and combining values (see *Jalca*, **47,** 629) has the following faults: (a) no correction is made for untanned hide powder dissolved and lost during washing; (b) temperature during shaking is not controlled; (c) washing may be incomplete because of channelling; (d) drying the powder is very slow, requiring about a week; (e) the results with hide powder do not agree with those found in practice. The following method is proposed: Tan in a 3-neck flask provided with a stirrer rotating at 150 rpm. Immerse the flask in a water bath regulated to 20°C. Instead of hide powder use 1-cm. squares of acetone-dehydrated calfskin prepared by the method of Naumann (*Jalca*, **49,** 125); this material does not require washing before use. Soak a quantity of hide containing 2 g. of hide substance for 2 hours in 50 ml. of water, then add 20 ml. of 6% tannin solution and, at hourly intervals, two 15 ml. portions of the tannin solution. Tan for 24 hours, then remove an aliquot for analysis. Wash the leather in the flask by passing 3 liters of water, at the rate of one liter per hour, in through one of the necks and out another, closing the latter with a screen to retain hide pieces. Collect the wash water. Centrifuge, dry, and weigh aliquots of the tannin solution, the detanned solution, and the wash water, and from these calculate tan (TV) and combining (CV) values. Air dry the hide material for further investigation. The pieces make possible a good evaluation of leather quality. This method gives reproducible results that are

available in 48 hours and can be used for control work. Some typical results by the old (Strather-Herfeld) and the new methods are shown in the following table for laboratory-prepared syntans and other tanning materials.

Tanning Materials	Old Method TV	Old Method CV	New Method TV	New Method CV	Shrinkage Temp. °C.
Sulfonated Novolak	65	41	41	31	78
Condensed dihydroxydiphenylsulfone and sulfite waste liquor	65	32	47	43	68
Sulfited Novolak and sulfite waste liquor	58	31	39	35	68
Auxiliary syntan	43	16	36	18	68
Sulfite waste liquor	47	24	27	25	67
Spruce extract	72	51	60	54	80
Quebracho extract	104	63	65	56	86

By the new method there is a large difference between the TV and CV values for the auxiliary syntan. For the sulfite waste liquor the difference is small, because the TV value is low. Shrinkage temperature is low if sulfite waste liquor is present. The take-up of an aromatic tannin depends on salt formation, activity of dipoles, or formation of hydrogen bonds. The greater the tendency is to form salts, that is, the more the tannin resembles an auxiliary tannin, the lower the pH value for maximum TV and CV values, as is shown in the following table.

Tannin	pH 2.0 TV	pH 2.0 CV	pH 3.5 TV	pH 3.5 CV	pH 4.5 TV	pH 4.5 CV
Spruce extract	61	58	59	54	56	50
Sulfonated Novolak	43	36	41	31	40	31
Auxiliary syntan	38	27	36	17	24	14
Sulfite waste liquor	33	32	27	25	21	21

In a test with mixtures of a replacement syntan and sulfite waste liquor, it was found that quality decreased only when 40 per cent or more of sulfite waste liquor was used. I.D.C.

Laboratory Testing of Pancreatic Bates. W. W. Bryce, E. Burbidge, and M. Horwood. *J. Soc. Leather Trades' Chemists*, **40,** 3 (1956).—The casein digestion method for enzyme bate evaluation (particularly as suggested by E. Lend and H. S. Owen, *J.S.L.T.C.*, **37,** 22 [1953]) was examined. The authors consider that activity of bates can be directly assessed by their power to digest casein. They suggest that 50 trypsin units (T.U.) be defined as that quantity of pancreatic proteinase capable of digesting 50 mg. of protein nitrogen in a 5-percent casein solution at pH 8.2 in one hour at 40°C. Rather than bringing pancreatic proteinase into solution by solubilizing it, electrolytes are said to act as desorbing agents in eluting proteinase from a strongly adsorbing medium (wood flour). The suitability of a salt extraction method for general application to bates and enzymates in order to prepare enzyme test solutions is questioned. In the presence of wood flour it is considered necessary to restrict the hydrolysis of casein if accurate evaluation of a bate is to be made. For

routine testing of bates and as an alternative to the soluble nitrogen determination method, a procedure employing nitrocasein as a substrate is recommended. The enzyme attacks the nitrocasein; unchanged protein is precipitated and the filtrate treated with dilute NaOH solution. The yellow color developing is proportional to the amount of nitrocasein in solution and to enzyme activity. The color is estimated by visual comparison with prepared standards or in a colorimeter. Preparation of nitrocasein (after von Pechmann, *Biochem. Zeitschr.*, **321**, 248 [1950]) is given in detail. Assays of a series of enzymates using both casein and nitrocasein as substrates gave good agreement. J.M.C.

Ion Exchange Resins and Their Application in Leather Chemistry. K. W. Pepper. *J. Soc. Leather Trades' Chemists*, **40**, 17 (1956).—An account is given of the structure and general behavior of ion exchange resins, apparatus required, and practical methods of using them. A table lists the equivalent ion exchange resins produced by three manufacturers. Under practical methods is included a discussion of particle size and pretreatments of resins. The applications of ion exchange of interest to leather chemists are: (a) industrial scale; (b) routine chemical analysis; and (c) research on proteins and tanning materials. On the industrial scale, ion exchange processes are economically most attractive either for replacement or removal of ionic impurities occurring in small amounts in water or in an organic nonelectrolyte. The use of ion exchange in the determination of salts in tan liquors is mentioned. Application of ion exchange resins to aminoacid analysis and to estimation of positively and negatively charged complex ions in chrome liquors is described. J.M.C.

Comparison of Methods for Determining the pH of Chrome-Tanned Leather. R. L. Sykes. *J. Soc. Leather Trades' Chemists*, **40**, 30 (1956).—The Atkin-Thompson method of determining the apparent acidity of chrome-tanned leather is compared with that used by the American Leather Chemists' Association. Slightly higher standard deviations were observed with the Atkin-Thompson procedure on the series of leathers analyzed. Data obtained from pH measurements of 100 leather samples from a great many sources showed a linear relationship between the measurements of A.L.C.A. acidity and the Atkin-Thompson figure. The greater simplicity of the A.L.C.A. method makes it particularly attractive for routine testing. J.M.C.

Line Processing of Cattle and Pork Skins. A. Anfimov and V. Tsibanaova. *Myasnaya Ind. S.S.S.R.*, **26**, No. 5, 22 (1955); *Chem. Abstr.*, **50**, 2997*h* (1955).—The salting of hides and skins in a continuously conveyed system is described. The relation of salt pickup to time, and relation of drying to time, at temperatures of 18°-20°, 30°, and 35°C., is plotted.

The Mechanism of the Formation and Decomposition of Sulfides, Polysulfides, Sulfites and Thiosulfates. E. Schulek and E. Körös. *Acta Chim. Acad. Scientarium Hungaricae*, **3**, 125-38 (1953) (in German); *Hungarian Tech. Abstracts*, **6**, 115 (1954) (in English).—Sulfur dissolves in hot NaOH or aqueous NH_3 forming sulfide, polysulfide and thiosulfate. The solutions are quickly oxidized by atmospheric oxygen forming sulfite and thiosulfate; the latter is oxidized in part to tetrathionate. Alkaline salts, e.g., Na_3PO_4 and $Na_2B_4O_7$, dissolve small amounts of sulfur. H.B.M.

Determination of Sulfide Sulfur in Inorganic Compounds Containing Sulfur in Various Forms of Bonds. F. Schulek and E. Körös. *Acta Chim. Acad. Scientiarum Hungaricae*, **3**, 111-23 (1953) (in German); *Hungarian Tech. Abstracts*, **6**, 114 (1954) (in English).—Analysis is carried out in a solution free of oxygen. H_2S is determined by distillation from boric acid solution into Br water, and HBr is titrated after expelling

excess Br. In the presence of polysulfide the precipitated S can be eliminated as KCNS by adding KCN. By using an accurately known excess of KCN, polysulfide can be determined in the presence of sulfide. H.B.M.

Determination of Sulfur by Wet Combustion with Perchloric Acid. Per Olof Bethke. *Anal. Chem.*, **28,** 119-22 (1956).—The sample is oxidized with nitric and perchloric acids in a special apparatus to avoid loss of SO_3. Sulfate may be determined by the gravimetric procedure, but much time is saved by reducing to H_2S with a mixture of hydriodic, hypophosphorous, and hydrochloric acids, distilling in a current of nitrogen, absorbing the H_2S in NaOH, and determining it iodimetrically. The original paper should be consulted for details of apparatus and procedure. The method gave recoveries varying from 98.7 to 101.4% for 12 supposedly pure sulfur compounds. Leather and calf hair yielded 1.61 and 3.77% S respectively by this method, compared to expected values of 1.50 and 3.66%. H.B.M.

The Effect of Buffer and Electrolyte on the Diffusion of an Acid Dye in Gelatin. R. B. Pontius, M. L. Kaplan, and R. M. Husney. *J. Phys. Chem.*, **60,** 9-12 (1956).—A freeze-drying technique for measuring diffusion of dyes in gelatin on a microscopic scale has been used to measure the diffusion of an acid dye in gelatin. The method consists of dyeing a sample of a thin gelatin coating, arresting the diffusion by rapidly freezing the sample, dehydrating and sectioning the sample, and making micro-densitometer measurements of dye density as a function of penetration. The effects of adding buffers and electrolytes to the dye bath have been studied. It is shown that maximum concentration of dye in the gelatin, which is very much greater than that in the dye bath, apparently is not reached at the gelatin surface immediately at the start of dyeing. Difficulties in the computation of numerical values of the diffusion coefficients resulting from the time-dependent surface concentrations are discussed. All dyeings were made at pH 4.0 with Brilliant Alizarin Light Red B. Addition of buffers (acetate-citrate or acid phthalate) increased the initial rate of dyeing but retarded the subsequent rate. Dyeing was retarded further by addition of NaCl to the acid phthalate buffer. H.B.M.

Determination of Silicones in Textile Materials. Gerald M. Petty. *Anal. Chem.*, **28,** 250-1 (1956).—Extraction of the silicone from textiles by means of solvents gave low results, because of partial polymerization and insolubilization. Dry-ashing is not permissable because some of the silicone is volatilized. The sample should be wet-ashed with a mixture of sulfuric and nitric acids, followed by perchloric acid after most of the organic matter is destroyed. SiO_2 is then determined by conventional methods. The factor for converting SiO_2 to silicone depends upon the particular silicone that is present. H.B.M.

Determination of Aldehydes by Mercurimetric Oxidation. James E. Ruch and James B. Johnson. *Anal. Chem.*, **28,** 69-71 (1956).—This method is based on the oxidation of aldehyde to acid by mercuric ion, which in turn is reduced to free mercury. The free mercury is measured iodimetrically. The method is applicable to the determination of virtually any concentration of aldehyde in the presence of most acids, alcohols, esters, acetals, ketones, ethers, organic chlorides, and epoxides. Determinations of purity of 12 different aldehydes checked well with results by the hydroxylamine procedure. For details of the procedure, which are important, the original paper should be consulted. H.B.M.

Red Spots on Chrome Leather. H. Bartram and C. Riess. *Das Leder*, **6,** 219 (1955).—Chrome-tanned, split, cattle-hide leather from overseas was found upon receipt to be covered with red spots. The spots averaged about 1 cm. in diameter and extended entirely through the leather from grain to flesh. The spots were caused by a mold of the Monoverticillium

group and the Penicillium family. It resembled the Catenularia Grove family, but could not be identified as *C. fuliginea syn. P. simplex*. Its morphology is given. It was isolated on acid wort agar and grew at either 20° or 30°C. It could be transferred to normal chrome leather where it formed red spots in 8 days which increased in intensity for 2 or 3 weeks. It could also be grown on vegetable leather and filter paper in a humid chamber at 20°, but not at 30°C. I.D.C.

Industrial Statistics. Wm. Volk. *Chem. Eng.*, **63,** No. 3, 165-90 (1956).—This is a description, in simple language and with abundant examples, of the application of statistical techniques to chemical engineering data. H.B.M.

The National Leathersellers College. J. P. Danbury. *Chem. & Ind.*, 71-4 (1956).—This institution, founded in 1909 as the Leathersellers Technical College, became the (British) National Leathersellers College in 1951, supported in part at least by the British Ministry of Education. Its facilities have been enlarged and modernized, enabling the students to work through all kinds of leather from start to finish, using commercial equipment. The theoretical "capacity" is 12 heavy hides and 600 light skins per week. Ample laboratories are provided, both for teaching and research. The college attracts students from all over the world; most, but not all, have had some previous contact with the leather industry. The standard course runs for 2 years, and may soon be extended to 3 years. Numerous specialized short courses and refresher courses are offered. Selected graduates are invited to remain for an additional year to carry out research. Courses in the administrative and managerial aspects of the leather industry may be added soon. Close cooperation is maintained with industrial research organizations and with the Leather Industries Department of Leeds University. H.B.M.

Leather from Packing House Pigskins. Anon. *Rohm and Haas Reporter*, **14,** No. 1, 7-11 (1956).—Although the 70 million hogs slaughtered annually in the United States are said to represent potential raw material for half a billion square feet of leather, very few of these skins reach the tanneries, and then only as narrow strips, because hand flaying is prohibitively expensive. A machine has been developed for flaying half carcasses, yielding skin pieces averaging 3½ square feet, uniform in thickness and free from bristles. One tannery is said to be receiving 100,000 lb. of this stock weekly, and may produce 10 million feet of pig leather this year. H.B.M.

The Skin and Leather of Marine Animals. V. Expressible Water in Shark Skin. Toyoo Takahashi. *Bull. Japan Soc. Sci. Fisheries*, **18,** 341-8 (1952-3); *Chem. Abstr.* **50,** 3786*g* (1956).—When green shark skin was pressed, the relation between expressible water (W), pressure (P), and initial water content (W_0) was found to be: $dW/dP = K(W_0-W)/P$. The curve had an inflection point at P=5–7 kg., and the skin became transparent at nearly the same pressure. Methylene blue dissolved easily when placed on fresh skin (70-80% water), but not when placed on the pressed, transparent skin (about 45% water). The same equation held for moist cotton, but here there was no inflection point. The water expressed at pressures below the inflection point seems to be present between the fiber bundles, and that expressed above the inflection point seems to be present in the interfibrillary spaces within the bundles.

Tanning Materials of the British Commonwealth. Mangrove Bark. R. W. Pearman. *Colonial Plant and Animal Products*, **5,** 96 (1955).—The species of mangrove found in various countries of the commonwealth are described, with statistics on exports of bark and extract, and imports into the U.K. H.B.M.

Hopea Parviflora Bark as a Substitute for Imported Wattle Bark. P. S. Chowdary, K. A. Joseph and K. Padmanabhan. *Tanner (India)*, **10**, No. 6, 17-20 (1955).—This is a large tree, much used for lumber. The bark is plentiful and cheap. It contains 20-26% tannin and 6-9% soluble non-tannin (10% water basis). When used alone, *H. parviflora* bark yielded leather of rather low degree of tannage, but a 2:1 blend with myrobalans gave excellent leather. H.B.M.

Chrome Upper Production in East Pakistan. Syed Mustafizur Rahim. *Tanner (India)*, **10**, No. 7, 14-20 (1955).—An interesting account of procedures employed. H.B.M.

PATENTS

Coating Leather; Finishing and Pasting Drying of Leather. Brit. Pat. 717,883. Badische Anilin- & Soda- Fabrik. Apl. July 4, 1952 [July 11, 1951; Dec. 1, 1951], No. 16824/52. Classes 76 and 140. [Also in Group IV (a)]. Leather is coated with a colloidal solution of an ammonium salt of a carboxyl group-containing copolymer of an acrylic or methacrylic acid ester in a mixture of water and an organic solvent miscible with water. Copolymers are those of methyl, ethyl, propyl or butyl esters of acrylic or methacrylic acid with acrylic, methacrylic, maleic, or crotonic acids, having 5–35 per cent unesterfied carboxyl groups. The organic solvents may be ethyl, methyl, or propyl alcohols, acetone or tetrahydrofurane and the solvent mixture may contain 60–150 parts organic solvent per 100 parts copolymer. The resulting solutions may contain aqueous colloidal solutions of casein, albumen, or pectin, or water dilutable leather pigment finishes containing a pigment, e.g. iron oxide red, and hardenable or non-hardenable film-forming binding agents, e.g. casein, shellac, carnauba wax, or nitrocellulose. Drying oils, e.g. linseed oil, or sulphonated castor oil plasticizer may be added to the solutions. Alternatively, the copolymer solutions may be applied to leather already coated with a pigment finish or a pigment finish may be applied to the copolymer coating. The copolymer coatings may be utilized in the "pasting drying" of leather, wherein the leather is stuck to a metal, enamelled metal, or glass plate, by the copolymer solution, smoothed and dried, e.g. for five hours at 55° C. The dried leather may be finished without washing off the coating.

Unhairing Hides. Brit. Pat. 717,642. Berka, E. Apl. Sept. 16, 1952 [Sept. 25, 1951], No. 23276/52. Class 76. An unhairing agent for hides and skins is prepared by allowing fish or fish waste to undergo autolysis at 15°–40° C., the liquid subsequently obtained being separated from bones, scales, etc. and stabilized by the addition of alkaline substances, particularly calcium hydroxide. Alternatively the liquid is stabilized by mixing it with a pre-dried absorbent such as sawdust or bentonite to give a dry-feeling product. The latter may either be mixed with dry alkaline agents before storing or may be mixed with an alkaline agent in aqueous solution shortly before use. To accelerate the unhairing process the hides or skins are preferably pre-treated with dilute sodium hydroxide solution.

Impregnating Paper and Leather. Brit. Pat. 717,144. Soc. pour le Traitement et l'Amelioration des Tissus. Apl. Feb. 6, 1952 [Feb. 7, 1951], No. 3162/52. Classes 76 and 96. [Also in Group IV (c)]. The resistance to abrasion of fibrous materials, e.g. paper, cardboard or leather, is improved by impregnating them with a silicic acid ester containing only ester groups attached directly to the silicon atom, hydrolysis of the ester being substantially prevented before impregnation, and then heating to deposit silica in the fibers. Specified esters are methyl, ethyl, propyl, and octyl silicates. The ester may be applied alone or as a solution in, for example, benzine, toluene, trichlorethylene, or an alcohol, or as an aqueous emulsion.

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MYRTAN

A TANNING EXTRACT

made from the wood of an Australian species of the Eucalyptus family. It contains both catechol and pyrogallol tannin, the latter predominating.

TYPICAL A.L.C.A. ANALYSIS

	Ordinary	Clarified
TANNIN	61.55	64.34
NON-TANNIN	16.03	17.14
INSOLUBLES	1.70	0.72
WATER	20.72	17.80

As a retanning agent for chrome tanned leather, Myrtan possesses many advantages, such as smooth and strong grain, good color and break, as well as a round feel.

Blended into sole leather tannages, it has given better yields and improved color.

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Mutual's name for their basic chromic sulfate used in one-bath chrome tanning. Available in two grades with approximate analyses as shown below.

	Koreon M	Koreon X
Cr_2O_3	24%	25%
Basicity (Schorlemmer)	33%	32%

Koreon is packed in multi-wall paper bags containing 75 pounds, and in fibre drums containing about 325 pounds.

SODIUM BICHROMATE POTASSIUM BICHROMATE

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